

Fall 1999

Finite fraction method for tracking disinfection by-product precursors in water treatment

Doanh Van

New Jersey Institute of Technology

Follow this and additional works at: <https://digitalcommons.njit.edu/dissertations>



Part of the [Civil Engineering Commons](#)

Recommended Citation

Van, Doanh, "Finite fraction method for tracking disinfection by-product precursors in water treatment" (1999). *Dissertations*. 437.
<https://digitalcommons.njit.edu/dissertations/437>

This Dissertation is brought to you for free and open access by the Theses and Dissertations at Digital Commons @ NJIT. It has been accepted for inclusion in Dissertations by an authorized administrator of Digital Commons @ NJIT. For more information, please contact digitalcommons@njit.edu.

Copyright Warning & Restrictions

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specified conditions is that the photocopy or reproduction is not to be “used for any purpose other than private study, scholarship, or research.” If a user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of “fair use” that user may be liable for copyright infringement,

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

Please Note: The author retains the copyright while the New Jersey Institute of Technology reserves the right to distribute this thesis or dissertation

Printing note: If you do not wish to print this page, then select “Pages from: first page # to: last page #” on the print dialog screen

The Van Houten library has removed some of the personal information and all signatures from the approval page and biographical sketches of theses and dissertations in order to protect the identity of NJIT graduates and faculty.

ABSTRACT

FINITE FRACTION METHOD FOR TRACKING DISINFECTION BY-PRODUCT PRECURSORS IN WATER TREATMENT

by
Doanh Van

Dissolved Organic Matter (DOM) has been the subject of recent regulatory activities and agenda. Among them are the Information Collection Rule (ICR), the Disinfectants/Disinfection By-Product Rule (D/DBPR) and the Interim Enhanced Surface Water Treatment Rule (ESWTR). Both the latter two have provisions to limit the formation of disinfection by-products (DBP) by controlling reactivity and removal of DOM or both. Brief regulatory review of these rules was given.

Although the topic of DBP formation potential and DBP precursor removal have been studied by many researchers since Rooks (1974), the efficacy of methods that have been developed to date has been handicapped by the notion that DBP precursors can be, and have been, represented by the surrogate parameter TOC, which is aggregate in nature. To contribute to the current knowledge concerning DBP precursors and their formation potential, the objectives of this research were to develop a rapid method for the identification of DBP precursors, establish a DBP formation potential database and correlations, and develop computer codes to be used as a toolkit to facilitate the investigation of DBP precursors and formation potential.

In this research, finite fraction method (FFM) was used to isolate and fractionate DOM from locations within three water treatment plants (WTP) which draw water from two different sourcewaters in north and central New Jersey. A resin adsorption method

was used to fractionate and isolate six fractions. Operationally, these fractions were termed: hydrophobic acid, hydrophobic neutral, hydrophobic base, hydrophilic acid, hydrophilic neutral and hydrophilic base. Fraction mass balance confirmed the effectiveness of the method.

Each fraction was subjected to a 7-day chlorine disinfection by-product (DBP) formation potential test at standard condition of pH 7 and temperature of 25 deg. C. Results showed that all fractions are DBP precursors and that each fraction has different reactivity levels to the formation of the three classes of DBPs which are trihalomethanes (THMs), haloacetonitriles (HANs) and haloacetic acids (HAAs). The hydrophilic acid and hydrophobic neutral fractions were found to be the most problematic precursors to the formation of THM and HAA DBPs, respectively.

Spectral Fluorescent Signature (SFS) is a process of subjecting each reasonably finite component (or fraction) of DOM to fluorescence scanning to produce unique spectral fluorescent characteristic of signature (hence the term SFS). SFS method was investigated and developed to rapidly identify the various fractions of DOM. It was found that (1) each fraction fluoresces uniquely in certain region of the 3-D spectrum, (2) the fraction identification was a function of the fluorescent intensity, the slope of fluorescence peak and the area under the peak spectrum. In fact, it was found that the product of the spectral slope and the spectral area establishes a shape factor (SF) that is unique to give the fraction an identifiable digital signature.

Computer codes were developed using graphical user interface (GUI) features to facilitate rapid identification of DBP precursors and computation of the corresponding

formation potential by iterative method in searching the databases. Method validation was conducted. Good correlations were achieved.

The variation of each DBP precursor throughout the treatment train of the water treatment plant was also examined to provide insight into the effectiveness of the unit operation with regard to the removal of the precursor. For most precursors, coagulation and sedimentation units appeared to be most effective in the removal. For the problematic precursors however, such unit processes did not seem to be as effective.

**FINITE FRACTION METHOD FOR TRACKING
DISINFECTION BY-PRODUCT PRECURSORS
IN WATER TREATMENT**

**by
Doanh Van**

**A Dissertation
Submitted to the Faculty of
New Jersey Institute of Technology
In Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy**

Department of Civil and Environmental Engineering

January 2000

Copyright © 2000 by Doanh Van
ALL RIGHTS RESERVED

APPROVAL PAGE

FINITE FRACTION METHOD FOR TRACKING DISINFECTION BY-PRODUCT PRECURSORS IN WATER TREATMENT

Doanh Van

Dr. T. Marhaba, Dissertation Advisor Assistant Professor of Civil and Environmental Engineering, NJIT	Date
--	------

Dr. R. Dresnack, Committee Member Professor of Civil and Environmental Engineering, NJIT	Date
---	------

Dr. H-N Hsieh, Committee Member Professor of Civil and Environmental Engineering, NJIT	Date
---	------

Dr. R. Luo, Committee Member Assistant Professor of Chemical, Chemistry and Environmental Science, NJIT	Date
--	------

Dr. J. Schuring, Committee Member Acting Chairman & Professor of Civil and Environmental Engineering, NJIT	Date
---	------

BIOGRAPHICAL SKETCH

Author: Doanh Van

Degree: Doctor of Philosophy

Date: January 2000

Education: Doctor of Philosophy in Civil Engineering
New Jersey Institute of Technology, Newark, NJ, 2000

Master of Science in Civil Engineering
New Jersey Institute of Technology, Newark, NJ, 1995

**Professional
Registration:** Licensed Professional Engineer in New Jersey since 1986

**Scholastic &
Professional
Honor Societies:** Elected to National Honor Society Phi Kappa Phi (UIC)
Elected to National Honor Society Alpha Epsilon Lambda (NJIT)
Member of American Nuclear Society
Member of American Society of Mechanical Engineers
Member of American Water Works Association

Employment: Senior Manager, Environmental Technology & Energy
Warner Lambert Company, Morris Plains, NJ (1992-present)

Project Engineer
AlliedSignal Inc., Morristown, NJ (1986 – 1992)

Technical Staff Engineer
GPU Nuclear, Parsippany, NJ (1984-1986)

Nuclear Test and Startup Engineer
Commonwealth Edison, Chicago, IL (1981-1984)

Publications and Presentation:

1. **Marhaba, T.F., Van, D., and Lippincott, R.L. (1999)** "Rapid Identification of Dissolved Organic Matter Fractions in Water by Spectral fluorescent Signatures," *Water Research*. Accepted for publication.
2. **Marhaba, T.F., and Van, D. (1999)** "Chlorinated Disinfection By-Product formation Potential of Dissolved Organic Matter Fractions at an Ozonation Water Treatment Plant," *Advances in Environmental Research*, (3) 3, 255-268.
3. **Marhaba, T.F., Van, D., and Lippincott, R.L. (1999)** "Characterizing Dissolved Organic Matter Fractions Using Spectral Fluorescent Signatures And Post Processing By Principal Component Analysis," *Fresenius Journal of Analytical Chemistry*. Accepted for publication.
4. **Marhaba T.F., Van D. and Lippincott R.L. (1999)** "Changes in NOM Fractionation Through Treatment: A Comparison of Ozonation and Chlorination", *Ozone Sci Eng*. Accepted for publication.
5. **Marhaba, T. F., Van, D., and Lippincott, R. L. (1998)** "Effects of Ozonation vs. Chlorination Water Treatment Operations on Natural Organic Matter Fractions," *Proceedings of the 1998 Int. Ozone Assoc. Ann. Conf.*, Vancouver, B.C, Canada, pp. 363-382, October 18-21, 1998.
6. **Marhaba, T.F., Pipada, N.S., Van, D. (1998)** "Modified resin adsorption fractionation method for characterization of source water organics, *Proc. Am. Water Works Assoc. Source Water Symp.* October 28-31, 1998, San Francisco, CA.

This dissertation is dedicated to my enduring wife, Thủy-Mai,
and my 2 children Văn Lang and Văn Minh.

ACKNOWLEDGEMENT

The author sincerely expresses profound gratitude to his dissertation advisor, teacher and committee Chairman Dr. T. Marhaba. Simply put, this work could not have been done without his support, his unrelenting drive and pressure and his being visionary in academic research.

The author also extends his acknowledgement and genuine appreciation to the PhD Advisory Committee Members: Dr. R. Dresnack—the man who extols teaching, Dr. H-N Hsieh—the accomplished man who practices humility, Dr. R. Luo—the man who helps the student whom he knows not, and Dr. J. Schuring—the man whose principle interest is in the learning of his students. To all on the Advisory Committee, this student can proudly say “their scholarly credentials lend credence to my degree”.

The author would like to also thank his management: Director D. Patterson, Vice President J. Lime and Vice President Dr. A. Falk of Warner Lambert Company for their unparalleled support of higher education for this employee. Heartfelt thanks are also being extended to NJIT and NJDEP for their funding of this research; Clint Brockway for his much-needed technical assistance with the variety of equipment in the analytical laboratory; Matt, Neeraj, Sonu, Niket and Muhamad for their being colleagues and “lab-mate” during this long endeavor.

TABLE OF CONTENTS

Chapter	Page
1 INTRODUCTION.....	1
2 BACKGROUND.....	10
2.1 Regulations.....	10
2.1.1 Information Collection Rule (ICR).....	11
2.1.2 Enhanced Surface Water Treatment Rule (ESWTR).....	14
2.1.3 Disinfectant/Disinfection By-Product Rule (D/DBPR).....	15
2.2 Chemistry and Processes of Water Disinfection.....	17
2.2.1 Chlorine.....	17
2.2.2 Chloramine.....	19
2.2.3 Chlorine Dioxide.....	20
2.2.4 Ozonation.....	20
2.2.5 Ultra-Violet (UV) Light.....	22
2.2.6 Titanium Dioxide Photocatalysis.....	22
2.3 Formation of Disinfection By-Products.....	23
2.4 Health Risks Associated with each DBP.....	26
2.5 Related Prior Researches.....	25
2.6 Characterization of Natural Organic Matter (NOM).....	32
2.6.1 Humic Substance.....	33
2.6.2 Nonhumic Substance.....	34
2.7 Treatabilities Regarding DBP Precursor Removal.....	35

TABLE OF CONTENTS (Continued)

Chapter	Page
2.8 Correlations Regarding DBP Formation Potential.....	36
3 OBJECTIVES.....	39
3.1 Development of Spectral Fluorescent Signature Method for Rapid Identification of Targeted THMs and HAA Precursors.....	40
3.2 Development of Gas-Chromatography (GC) Generated DBP FP Database.....	40
3.3 Development of a Computer-Based Predictive Tool to Calculate DBP FP from SFS Reading of Raw Water Sample.....	40
4 MATERIALS AND METHODS.....	42
4.1 Participating Water Treatment Plants.....	42
4.2 DOM Isolation and Fractionation.....	48
4.3 Dissolved Organic Carbon (DOC) Analysis.....	53
4.4 DBP FP Test.....	54
4.5 DBP FP analyses by Gas Chromatography.....	55
4.6 SFS Analyses by Fluorescence Spectrophotometer.....	56
5. METHOD DEVELOPMENT FOR DOM PRECURSOR IDENTIFICATION AND DBP FORMATION POTENTIAL COMPUTATION.....	58
5.1 Identification of DOM Fractions Using SFS.....	58
5.1.1 Determination of Fraction's Concentration by SFS.....	62
5.1.2 Computer Code Development.....	67
5.1.3. Method Validation.....	70
5.2 Determination of DBP of Raw Water by SFS-GC Database Cross-Linking.....	77

TABLE OF CONTENTS (Continued)

Chapter	Page
5.2.1 DBP FP Correlations.....	79
5.2.1.1 Trihalomethanes.....	81
5.2.1.2 Haloacetic Acids.....	82
6. RESULTS AND DISCUSSION.....	84
6.1 Fraction Mass Balance.....	84
6.1.1 The Effect of Treatment Processes.....	90
6.1.1.1 Variation of the hydrophobic base fraction.....	90
6.1.1.2 Variation of the hydrophobic acid fraction.....	92
6.1.1.3 Variation of the hydrophobic neutral fraction.....	93
6.1.1.4 Variation of the hydrophilic base fraction.....	94
6.1.1.5 Variation of the hydrophilic acid fraction.....	96
6.1.1.6 Variation of the hydrophilic neutral fraction.....	97
6.1.2 Aggregate vs. Fractionated DOC.....	99
6.2 Variation of DBP FP along the Treatment Train.....	100
6.2.1 The Effect of Treatment Processes.....	100
6.2.1.1 Variation of the hydrophobic base fraction.....	100
6.2.1.2 Variation of the hydrophobic acid fraction.....	102
6.2.1.3 Variation of the hydrophobic neutral fraction.....	104
6.2.1.4 Variation of the hydrophilic base fraction.....	106
6.2.1.5 Variation of the hydrophilic acid fraction.....	107

TABLE OF CONTENTS (Continued)

Chapter	Page
6.2.1.6 Variation of the hydrophilic neutral fraction.....	109
6.3 Validation of Results.....	111
6.3.1 Validation Using Water Samples from the Influent of the WTP.....	112
6.3.2 Validation Using Water Samples from the Basin of the WTP.....	115
6.3.3 Validation Using Water Samples from the Filtration of the WTP.....	119
6.3.4 Validation Using Water Samples from the Effluent of the WTP.....	123
6.4 Proposed Application of Precursor Removal Optimization Method.....	130
6.4.1 Sample Preparation.....	130
6.4.2 Fluorescent Spectrophotometer Preparation and Operation.....	131
6.4.3 Using the SFS Toolkit.....	131
6.4.4 Proposed Application of SFS Toolkit.....	132
6.4.5 Other Proposed Applications of the SFS Toolkit.....	134
7. CONCLUSION AND RECOMMENDATIONS.....	135
7.1 Conclusions.....	135
7.2 Recommendations.....	137
APPENDIX A FIGURES.....	139
APPENDIX B COMPUTER CODES.....	149
REFERENCES.....	323

LIST OF TABLES

Table	Page
1 ICR Monitoring Requirements.....	12
2. Disinfectants and Additional ICR Monitoring Requirements.....	12
3 Propose Phased-in of the D/DBP Rule.....	15
4 A Tabulation of Different Disinfection Processes and Their Resultant DBPs.....	24
5 DBP Grouping and the Associated DBP Constituents.....	25
6 Suggested Treatment Processes for Different Types of NOM Fractions.....	35
7 General Description of the Participating Water Treatment Plants and the associated Water Quality.....	47
8 Locations of the Six DOM Fractions Peaks.....	60
9 SFS Database of Individual Fractions.....	64
10 SFS-Concentration Correlations.....	65
11 Summary of Validated Results. Samples from EWC WTP.....	70
12 Summary of Validated Results. Samples from PVWC WTP.....	71
13 DBP formation potential of DOM fractions.....	78
14 Repeatability of Fractionation Procedure.....	84
15 Mass Balance of DOM Fractions along the Treatment Trains.....	85
16 Summary of the Hydrophobic Substances.....	98
17 Summary of the Hydrophilic Substances.....	98
18 Overall DOC and Precursor Removal.....	99

LIST OF TABLES (Continued)

Table	Page
19 Summary of Validated Results. Samples from Influent of the Canal Road Water Treatment Plant.....	112
20 Summary of Validated Results. Samples from Influent of the Passaic Valley Water Treatment Plant.....	114
21 Summary of Validated Results. Samples from the Sedimentation Basin of the Passaic Valley Water Treatment Plant.....	115
22 Summary of Validated Results. Samples from the Sedimentation Basin of the Canal Road Water Treatment Plant.....	117
23 Summary of Validated Results. Samples from the Sedimentation Basin of the Raritan Millstone Water Treatment Plant.....	118
24 Summary of Validated Results. Samples from the Filtration Unit of the Passaic Valley Water Treatment Plant.....	119
25 Summary of Validated Results. Samples from the Filtration Unit of the Canal Road Water Treatment Plant.....	120
26 Summary of Validated Results. Samples from the Filtration Unit of the Raritan Millstone Water Treatment Plant.....	122
27 Summary of Validated Results. Samples from the Effluent of the Passaic Valley Water Treatment Plant.....	123
28 Summary of Validated Results. Samples from the Effluent of the Canal Road Water Treatment Plant.	124
29 Summary of Validated Results. Samples from the Effluent of the Raritan Millstone Water Treatment Plant.....	126

LIST OF FIGURES

Figure	Page
1	Microbial Protection versus Chemical Exposure: a Delicate Balancing Act.....4
2	A Typical Water Treatment Plant Schematic.....7
3	Research Protocol.....43
4	Canal Road (CR) Water Treatment Plant.....44
5	Raritan-Millstone (RM) Water Treatment Plant.....45
6	Passaic Valley (PV) Water Treatment Plant.....46
7	Isolation of the Hydrophobic Base Fraction.....48
8	Isolation of the Hydrophobic Acid Fraction.....49
9	Isolation of the Hydrophobic Neutral Fraction.....49
10	Isolation of the Hydrophilic Base Fraction.....50
11	Isolation of the Hydrophilic Acid Fraction & Isolation of the Hydrophilic Base Fraction.....50
12	Contour of a Raw Water SFS and Major Regions Where Fractions' Peak Were Found to Be Unique When Examined Separately.....61
13	Spectral Fluorescent Signature (SFS) of a Typical Hydrophilic Acid Fraction at 0.4 ppm.....63
14	A Peak Spectrum of the Hydrophilic Acid Fraction at 0.4 ppm. Excitation Wavelength Was at 225 nm. SF Was 4.3.....64
15	An illustration of How the Spectral Slopes and Areas are Computed.....67
16	Flowchart of the Computer Codes.....68
17	Spectrum of the Hydrophobic Acid Fraction at 0.4 ppm Showing the Shape Factor SF and its Components.....71

LIST OF FIGURES (Continued)

Figure	Page
18 The Hydrophobic Acid Fraction at 0.4 ppm Shown on a Raw Water Intake Water Spectrum. SF Factors Are Being Match.....	
19 Spectrum of the Hydrophobic Base Fraction at 0.1 ppm Showing the Shape Factor SF and its Components.....	72
20 The Hydrophobic Base Fraction at 0.1 ppm Shown on a Raw Water Intake Water Spectrum. SF factors Are Being Matched.....	73
21 The Hydrophobic Neutral Fraction at 0.7 ppm Shown on a Raw Water Intake Water Spectrum. SF Factor Cannot be Matched. Correlation Was Being Used (figure 22).....	73
22 Fraction Concentration-Shape Factor Correlation Was Being Used for the Calculation Since There Was No Match in the SFS Database.....	74
23 Spectrum of the Hydrophilic Acid Fraction at 2 ppm Showing the Shape Factor SF and its Components.....	74
24 The Hydrophilic Acid Fraction at 2 ppm Shown on a Raw Water Intake Water Spectrum. SF factors Were Being Matched.....	75
25 Spectrum of the Hydrophilic Base Fraction at 0.1 ppm Showing the Shape Factor SF and its Components.....	75
26 The Hydrophilic Base Fraction at 0.1 ppm Shown on a Raw Water Intake Water Spectrum. SF Factors Were Being Matched.....	76
27 The Hydrophilic Neutral Fraction at 0.8 ppm Shown on a Raw Water Intake Spectrum. SF factor Cannot Be Matched. Correlation Was Being Used (figure 28).....	76
28 Fraction Concentration-Shape Factor Correlation Was Being Used for the Calculation Since There Was No Match in the SFS Database.....	77
29 Protocol for DBP FP Test and Liquid-Liquid Extraction Procedure.....	80
30 DOM Fraction Mass – Raritan Millstone plant.....	86

LIST OF FIGURES (Continued)

Figure	Page
31	DOM Fraction Mass – Canal Road plant.....87
32	DOM Fraction Mass – Passaic Valley plant.....88
33	Fraction Distribution in the Common Water Intake of the Canal Road and Raritan-Millstone Water Treatment Plant.....89
34	Fraction Distribution in the Intake Water of the Passaic Valley Water Treatment Plant.....90
35	A Comparison of the Variation of the Hydrophobic Base Fraction in the Ozonation Plant (Canal Rd) and the Chlorination Plant (RM).....91
36	A Comparison of the Variation of the Hydrophobic Acid Fraction in the Ozonation Plant (Canal Rd) and the Chlorination Plant (RM).....93
37	A Comparison of the Variation of the Hydrophobic Neutral Fraction in the Ozonation Plant (Canal Rd) and the Chlorination Plant (RM).....94
38	A Comparison of the Variation of the Hydrophilic Base Fraction in the Ozonation Plant (Canal Rd) and the Chlorination Plant (RM).....95
39	A Comparison of the Variation of the Hydrophilic Acid Fraction in the Ozonation Plant (Canal Rd) and the Chlorination Plant (RM).....96
40	A Comparison of the Variation of the Hydrophilic Neutral Fraction in the Ozonation Plant (Canal Rd) and the Chlorination Plant (RM).....97
41	Variation of the THM FP of the Hydrophobic Base Fraction along the Treatment Train (Ozonation vs. Chlorination Plant).....101
42	Variation of the HAA FP of the Hydrophobic Base Fraction along the Treatment Train (Ozonation vs. Chlorination Plant).....102
43	Variation of the THM FP of the Hydrophobic Acid Fraction along the Treatment Train (Ozonation vs. Chlorination Plant).....103
44	Variation of the HAA FP of the Hydrophobic Acid Fraction along the Treatment Train (Ozonation vs. Chlorination).....104

LIST OF FIGURES (Continued)

Figure	Page
45	Variation of the THM FP of the Hydrophobic Neutral Fraction along the Treatment Train (Ozonation vs. Chlorination).....105
46	Variation of the HAA FP of the Hydrophobic Neutral Fraction along the Treatment Train (Ozonation vs. Chlorination).....105
47	Variation of the THM FP of the Hydrophilic Base Fraction along the Treatment Train (Ozonation vs. Chlorination).....106
48	Variation of the HAA FP of the Hydrophilic Base Fraction along the Treatment Train (Ozonation vs. Chlorination).....107
49	Variation of the THM FP of the Hydrophilic Acid Fraction along the Treatment Train (Ozonation vs. Chlorination).....108
50	Variation of the HAA FP of the Hydrophilic Acid Fraction along the Treatment Train (Ozonation vs. Chlorination).....109
51	Variation of the THM FP of the Hydrophilic Neutral Fraction along the Treatment Train (Ozonation vs. Chlorination).....110
52	Variation of the HAA FP of the Hydrophilic Neutral Fraction along the Treatment Train (Ozonation vs. Chlorination).....111
53	Predicted Concentrations as Compared to Actual Concentration. Influent Water Sample of the CR plant (May 21, 1998).....113
54	Predicted Concentrations as Compared to Actual Concentration. Influent Water Sample of the PV plant.....114
55	Predicted Concentrations as Compared to Actual Concentration. Sedimentation Basin Water Sample of the PV plant.....116
56	Predicted Concentrations as Compared to Actual Concentration. Sedimentation Basin Water Sample of the CR plant.....117
57	Predicted Concentrations as Compared to Actual Concentration. Sedimentation Basin Water Sample of the RM plant.....118

LIST OF FIGURES (Continued)

Figure	Page
58 Predicted Concentrations as Compared to Actual Concentration. Filtration Water Sample of the PV plant.....	120
59 Predicted Concentrations as Compared to Actual Concentration. Filtration Water Sample of the CR plant.....	121
60 Predicted Concentrations as Compared to Actual Concentration. Filtration Water Sample of the RM plant.....	122
61 Predicted Concentrations as Compared to Actual Concentration. Effluent Water Sample of the PV plant.....	124
62 Predicted Concentrations as Compared to Actual Concentration. Effluent Water Sample of the CR plant.....	125
63 Predicted Concentrations as Compared to Actual Concentration. Effluent Water Sample of the RM plant.....	126
64 SFS methodology validation using composite data points at	128
65 Verification of THM FP (predicted vs. actual value).....	128
66 Verification of HAA FP (predicted vs. actual value).....	128
A1 Vacuum Filtration Setup to Transform Water Samples from TOC To DOC Using 0.45-um Filter Whatman Paper.....	138
A2 A Typical Soxhlet Extraction Setup for the Purification of DAX-8, AG-MP-50 and Duolite A7 Resin in Preparation for the DOM Fractionation Procedure.....	139
A3 A Three-Chromatographic Resin Adsorption Column Fractionation Setup.....	140
A4 A Peak Spectrum of the Hydrophobic Base Fraction at 0.1 ppm.....	141
A5 A Peak Spectrum of the Hydrophobic Base Fraction at 0.2 ppm	141
A6 A Peak Spectrum of the Hydrophobic Base Fraction at 0.4 ppm.....	142

LIST OF FIGURES (Continued)

Figure	Page
A7 A Peak Spectrum of the Hydrophobic Acid Fraction at 0.4 ppm.....	142
A8 A Peak Spectrum of the Hydrophobic Acid Fraction at 2 ppm.....	143
A9 A Peak Spectrum of the Hydrophobic Neutral Fraction at 0.1 ppm.....	143
A10 A Peak Spectrum of the Hydrophobic Neutral Fraction at 0.6 ppm.....	144
A11 A Peak Spectrum of the Hydrophilic Base Fraction at 0.1 ppm.....	144
A12 A Peak Spectrum of the Hydrophilic Base Fraction at 0.4 ppm.....	145
A13 A Peak Spectrum of the Hydrophilic Acid Fraction at 1 ppm.....	145
A14 A Peak Spectrum of the Hydrophilic Acid Fraction at 2 ppm.....	146
A15 A Peak Spectrum of the Hydrophilic Neutral Fraction at 0.6 ppm.....	146
A16 A Peak Spectrum of the Hydrophilic Neutral Fraction at 0.8 ppm.....	147

CHAPTER 1

INTRODUCTION

Demand of treatment of water for safe human use and consumption has never been more urgent than the era in which we are living today when urban centers are burgeoning and becoming over-populated. The economic engine, being driven primarily by industries, exerts tremendous pressure on the delicate multi-media environment with more and recalcitrant pollutants.

A real life case pointing to the critical need of water treatment and disinfection was the outbreak of cryptosporidium in the Spring of 1993 in Milwaukee which led to more than 100 fatalities and more than 400,000 people becoming sick (Mayohealth, 1999). This occurred not because there was no water treatment in place but because there was a malfunction in the treatment system.

Although the demand is greater today, the need for modern water treatment actually started at the dawn of the industrial revolution with the first treatment plant being built in 1829 in England. Evidence of primitive disinfection of water, however, was known much earlier in recorded history (Weber, 1972). Treatment in the early 19th century was simply by filtration of the Thames River water. Following the London cholera epidemic of 1854, people started to pay serious attention to the water that was extracted from their wells. It was not until 1892 that water treatment by filtration received a real life validation of its effectiveness. That year cholera epidemic, a waterborne disease, hit Hamburg, Germany disastrously because its water was not filtered. The proof of effective filtration was found in the nearby town of Altona, which

at the same time was left untouched by the epidemic primarily because the town's water was treated with filtration.

As beneficial as it was, the treatment of water in those early days only constituted treatment by filtration, which is a physical process. Disinfection is a process in which pathogenic organisms are destroyed or inactivated by the application of a strong oxidant into the water to be treated (Weber, 1972). This treatment of water by injecting chemicals into the water stream is a chemical process as opposed to just filtering water that was mentioned earlier.

In the early days of water treatment, however, slow filtration was the first treatment process, which later evolved into rapid filtration with the aid of coagulation and sedimentation process as the pre-treatment of water before the filtration units. Today the treatment of water, especially the disinfection aspect of it, spans the entire spectrum of processes known to us. Modern-day process to treat water in general takes on the form of Physico-Chemical-Biological treatment.

With 70,000 people dying each day from waterborne diseases (AWWA), and with new water supply being a costly commodity, it is imperative that we seek remedies to the problem within the bound of the existing water supply infrastructures. Treatment of water started to take on the meaning of disinfection of water.

Today in the United States, water supplies whose sources are drawn from surface water must receive filtration and disinfection treatment as required by the law (40 CFR 141.141.72). This is important because it has been estimated that more than 200 million Americans drink disinfected water every day. At a minimum, the disinfection treatment must be sufficient to ensure 99.9% inactivation of *Giardia lamblia* cysts and 99.99%

inactivation of viruses as required by the enhanced surface water treatment rule (ESWTR). This level of disinfection must be verified and documented every day as dictated by the regulations. To ensure this level of disinfection be achieved at all time, the law also requires that a minimum residual disinfectant concentration of 0.2 mg/l be maintained (40 CFC 141.141.72).

The three popular modes of disinfection being used today are ultraviolet light (UV), chlorination or its derivatives, and ozonation. Disinfection by one these processes or any combination thereof produces clear results that pathogens are either killed or made inactivated. While there is no argument about the benefits of disinfection with regard to the combat of waterborne diseases, there is no argument either about the risks that came into existence as a result of disinfection. Today, the issue of concern from the consumers is the disinfection byproducts (DBPs); the pressure on the authorities is to maintain a regulatory balance between DBPs and microbial protection; and the challenge for the engineers is to find the point of optimization to narrow down the regulatory domain (ref. figure 1). It turns out that disinfection of the water we drink requires a balancing act. On the one hand, chlorination has led to the eradication of cholera and typhoid fever and significant reduction of illnesses related to the intestine. On the other, it has been found that chlorinating the NOM-containing water does produce Disinfection By-Products which could be carcinogenic and/or mutagenic.

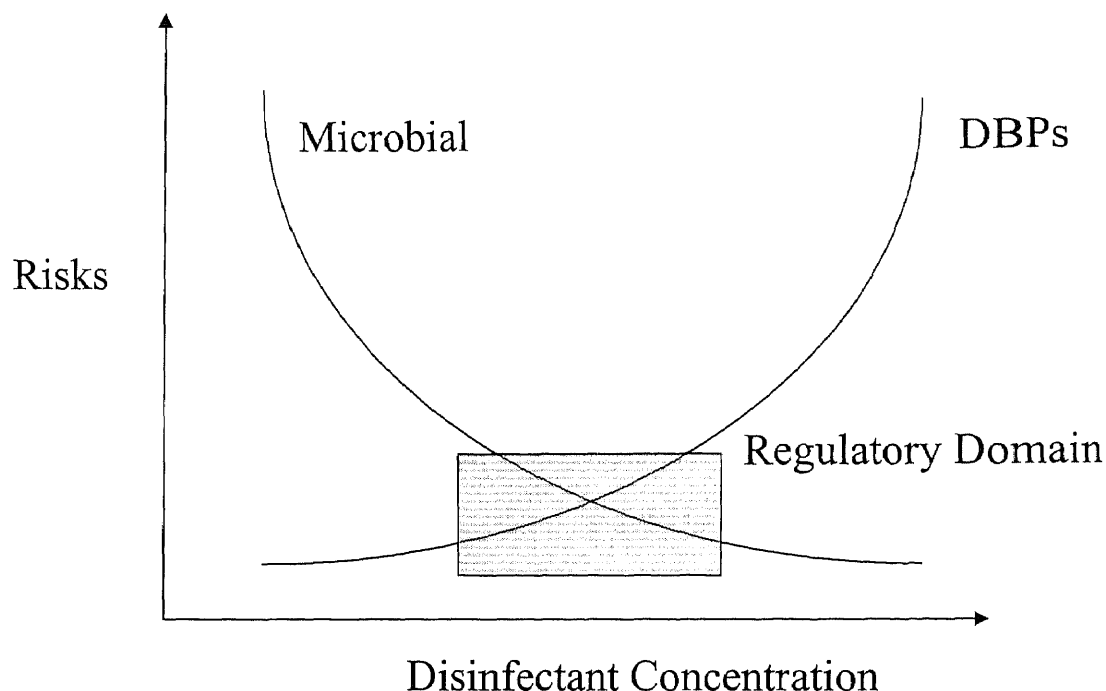


Figure 1 Microbial Protection versus Chemical Exposure: a Delicate Balancing Act (Lykins *et al*, 1994)

The discovery of DBPs, one of which was chloroform, in 1974 (Rook) and its implication to public health concerns as a direct result of chlorination of water for microbial protection has not stopped the wide-spread use of this disinfectant or its derivatives. Much effort has been undertaken in the scientific and engineering communities to study the health and safety aspects of these DBPs. Laws and regulations have been passed in the United States to put a limit on some of these DBPs. Major water utilities have been required to implement the Information Collection Rule (ICR), which was designed to establish scientific evidences and act as guideposts to charter new ways in the next phase in the dealing with DBP issue.

It is widely accepted that natural organic matter (NOM) or the dissolved portion of it--dissolved organic matter (DOM) in raw water is responsible for the formation of DBPs when the water undergoes disinfection, either by chlorination or ozonation. NOM or DOM comes into existence mostly as a result of vegetation decay that is washed into water bodies such as lakes and reservoirs. In fact, three strategies have been practiced in providing the remedies to the DBP issue. They are (1) remove NOM from the water prior to disinfection, (2) change to a different disinfectant that NOM would not have any reactivity with, and (3) remove DBPs once they have been formed. It is not possible to ascertain option 2 since different disinfectants may produce different DBPs that we may not yet comprehend the impact or are not able to detect. Option 3 is not practical because the formation of DBP is a function of time and because the points of treatment under this scenario is as numerous as there are consumers. At present, the most logical strategy is that of dealing directly with the removal of NOM. However, this presents the following problem of optimization: How much NOM should be removed that it makes sense economically? To what extent should the drinking public be protected chemically? Much effort has been devoted to the characterization of NOM, the different methods of correlating and predicting the formation of DBPs, and the different technologies in removing NOM, etc. All of these works took on the "component" approach in dealing with the problem (that is a solution of one variable is being kept independent of other variables of the problem). None has taken on the "system approach" or the approach in dealing with the optimization issue in the removal of NOM or the DBP precursors (that is seeking a solution of one variable but at the same time weighing its effect on other variables of the problem). This research is the first in taking this approach. The

following is the hypothesis of the dissertation: different constituents of NOM or DOM are responsible in varying degree in the formation of DBP. The optimization of the DBP precursor removal in water treatment, therefore, involves the rapid identification of the most problematic precursors and focused resources and prioritized treatment strategy in removing only these constituents.

The resulting optimization of DBP precursor removal is expected to yield less chemical dosage, minimized DBP formation, less dependence of supplementary GAC and membrane technology and, consequently, less costly to operate the water treatment plant. Costly retrofit of existing chlorinated water treatment plants to utilize other disinfection processes such as ozonation may be avoided.

A typical drinking water treatment plant starts with raw water intake from the river and progresses through rapid mix, flocculation, sedimentation, filtration and ends up with a clear well before the treated water is conveyed into the distribution system. Chemical is added along the way to provide treatment with respect to color, taste, odor, hardness, acidity, alkalinity, and disinfection. A schematic diagram of the treatment process is shown in figure 2 (Canal Road WTP of Elizabeth Water Company, NJ)

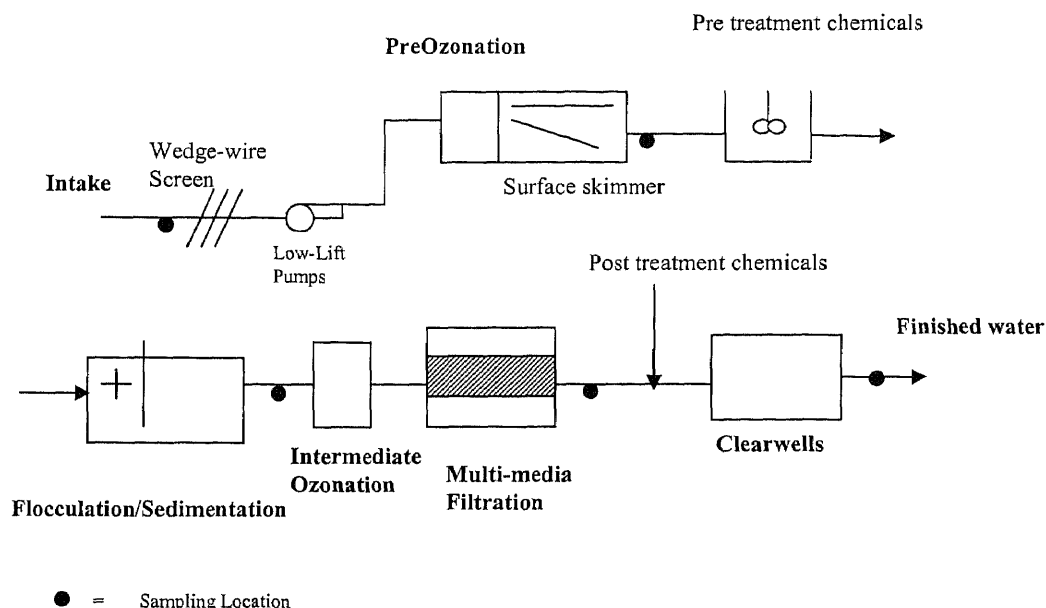


Figure 2 A Typical Water Treatment Plant Schematic. In Conventional Water Treatment Plant, Preozonation and Intermediate Ozonation Units Are Not Present

Until an ideal disinfectant can be found and put to work, chlorination is here to stay as an economical and powerful disinfection agent. Balancing act continues to be required.

The key to a successful balancing act lies in the optimization of the DBP precursor control. We must use the disinfectant as little as possible but not less!

It is obvious that one of the ways to head off the DBP-related public health problem is to remove the use of free chlorine. The issue then is how to deal with microbial contamination in the water, which is a more tangible and acute public health problem. If disinfection is a must then a need for a powerful and economical disinfectant necessitates the use of chlorine. Chlorine as a disinfectant will continue to be in high demand not only because of its powerful oxidizing and economical properties but also because its oxidation by-products are better understood than those from other alternative

disinfectants such as ozone, chloramines, chlorine dioxide, UV and potassium permanganate.

As long as chlorine remains in the disinfection equation, the question which is in much need of an answer for is how to minimize the formation of THMs and other harmful DBPs.

The dosage of chlorine is a function of the organic matter in water, which can exist naturally or artificially. One group of the man-made organic matter is called Synthetic Organic Matter or SOM. These are of small concentrations and are controllable by regulations. The other group of the man-made organic matter is the disinfection by products. Natural Organic Matter (NOM), on the other hand, comes from vegetative derivatives, soil corrosion, animal biodegradation and other debris. Since NOM exists in much greater proportion in water, it is the only category of organic matter that is being discussed in this work.

To date, NOM is generally characterized by its total organic carbon (TOC) or its UV absorbability. TOC is so widely used as a surrogate for NOM that DBP precursor removal has been made synonymous to TOC removal. Also, the required chlorine dosage has been correlated to the TOC concentration in the form of Cl_2 -to-TOC ratio or other empirical equations such as the following (Krasner, 1989) taking into account standard environmental conditions of pH of 7 and 25 deg. C temperature) :

$$\text{Cl}_2, \text{ mg/L} = 3 \times \text{TOC} + \text{NH}_3\text{-N}$$

The practice of correlating the chlorine and coagulant dosages based on TOC may have been acceptable up until now but with the growing concern for public health regarding the suspected carcinogenic THMs and other DBPs, this practice should be re-examined.

Another issue that stands on the way of optimization of DBP precursor removal is the long-lead analytical time in the fast changing nature of water environmental pollution. At present, the analytical results, which require about ten to fourteen days from the time of sampling, are as good as an academic exercise of a problem of the sourcewater whose environmental conditions were defined ten to fourteen days ago. There is a need to develop improved methods that are more responsive to the quantitative and qualitative dynamics of the sourcewaters. Isolation of NOM fractions, rapid identification of problematic DBP precursors and computation of the DBP formation potential constitute of scope of work of this research dissertation.

CHAPTER 2

BACKGROUND

2.1 The Regulations

Disinfection Byproducts are formed when disinfectants, while causing waterborne diseases to be almost eradicated, cause other problems related to human health at the same time. The disinfection byproducts may also be referred to as a “disinfection backfire” in layman’s term.

With regard to the harmful impact of the DBPs, the Environmental Protection Agency (EPA) made the following statement “public water systems use disinfectants to kill harmful microbial contaminants can cause illness, and may even be fatal for those with weak immune systems. However, disinfection and the resulting byproducts also pose risks, including potential increases in cancer rates and liver and kidney damage. The challenge is to strike an appropriate balance between these two risks so that public health is adequately protected.” (EPA 811-F-94-003 June 1994)

To perform this delicate balancing act, regulations had been proposed and are being implemented in the area concerning D/DBPs (i.e., the ICR) to ensure that disinfectants are adequately added to combat microbial contamination while, at the same time, minimizes risks of the public to be unnecessarily exposed to the chemicals.

The regulations regarding the D/DBP rule can be described as having the three components (Singer, 1994; Roberson *et al*, 1995). They are Information Collection Rule, Enhanced Surface Water Treatment Rule and Disinfectant/Disinfection By-Product Rule.

2.1.1 The Information Collection Rule

The D/DBPR and ESWTR apparently work to reduce the effect of one another. On the one hand, SWTR demands that disinfectant dosages and residual concentrations be high enough in the water to guard against the waterborne diseases caused by microbes. On the other hand, the D/DBP rule is to limit the amount of disinfectants and their residual levels to minimize harmful effect caused by the many DBP compounds. So how would the EPA know where to set the limits? The answer to this optimization problem lies primarily with the ICR.

The ICR was proposed on February 10, 1994 and was promulgated as a final rule on May 14, 1996 (61 FR 24354). It was made effective on June 18, 1996. This rule is intended to provide the EPA with information regarding the DBPs, pathogenic microorganisms and engineering data regarding the processes that each major Public Water System (PWS) is using to control the contaminants (chemical as well as microbial). With this information from the ICR database, the EPA will most likely revise the filtration and disinfection rule by proposing the D/DBP rule and the SWTR. ICR only was applicable to large PWSs serving at least 100,000 people (if water source is surface water) and 50,000 people (if groundwater is the source). ICR was to provide information for the enhancement of the SWTR via the Enhanced SWTR, which is the second component of the D/DBP rule. The information that each applicable PWS must monitor are DBPs, DBP precursors and other chemical parameters at specific locations throughout each treatment plant every month for 18 months. In addition, each applicable PWS shall characterize its treatment processes also on a monthly basis. This was to provide the engineering data of the current controls and treatment processes that are

being used. The ICR also requires each applicable PWS (except those that draw water from underground aquifers) to monitor and report the source water for cryptosporidium, *giardia*, total culturable viruses, total coliforms and fecal coliforms or E. Coli. The same must be monitored in the finished water when the contaminants exceed certain limits in the source water. Finally, the ICR requires certain PWSs to conduct treatment studies and monitor TOC at the inlet or outlet, depending on whether the source is surface or groundwater.

The ICR required that each PWS performed monthly and quarterly analyses of the following parameters, depending on where the samples were to be taken from:

Table 1 ICR Monitoring Requirements

Frequency	Water Quality Parameter
Monthly	pH, Alkalinity, Turbidity, Temperature, Calcium and Total Hardness, TOC, UV254, Bromide, Ammonia, Disinfectant residuals, Chlorine demand test
Quarterly	Total organic halides (TOX), THM ₄ , HAA _s , HAN, CP, HK, pH, Alkalinity, Turbidity, Temperature, Calcium and Total hardness, Disinfectant residual.

In addition to the above core requirements, depending on the type of disinfectant, the following are added to the list:

Table 2 Disinfectants and Additional ICR Monitoring Requirements

If the disinfectant is	Additional parameters to be monitored	Required frequency
Chloramines	Cyanogen chloride	Quarterly
Hypochlorite solution	Chlorate, free residual chlorine	Quarterly
Ozone	Bromide, bromate, ammonia, ozone residual.	Monthly
	Aldehydes, AOC, BDOC	Quarterly
Chlorine Dioxide	Chlorine dioxide residual, chlorite, chlorate, bromate, pH, Temperature	Monthly
	Aldehydes, AOC and BDOC	Quarterly

These DBP information are to be reported together with specific information requested of a PWS such as influent information, unit process information, information on the disinfectant used, its dosage, and the finished water distribution details.

The ICR not only directly affected the DBPs, it also affected the DBP precursor. As a consequence, applicable PWS must monitor TOC, THM_s and HAA_s and conduct DBP precursor removal studies (treatment studies) either by GAC or membrane process technologies.

The ICR protocol was extremely demanding (Nieminski *et al* 1996). It is apparently very costly to comply with also. The EPA estimated the cost of \$130 million would be needed in the area of monitoring the microbial contaminants and the disinfection by-products alone. It has been stated very succinctly that the ICR is probably the most significant nationwide effort to compile water quality data over a fixed time period.

2.1.2 Enhanced Surface Water Treatment Rule

The current SWTR (December 1990) together with the Total Coliform Rule (TCR) (June 1989) were intended to control pathogens in public water systems. SWTR requires 99.9% *giardia cysts* removal or inactivation and that for virus is 99.99%. This was to ensure that the finished water quality is not microbially compromised by the THM rule which established the 100 ppb MCL limit. SWTR also required the disinfectant residual level to be at least 95% of the distribution system. The proposed ESWTR (July 29, 1994; 59 FR 38832) will strive for the disinfection of *giardia cysts* and viruses above 3 log and 4 log, respectively, depending on the quality of the source waters. Currently, the interim ESWTR, which was proposed on July 29th 1994 and became effective in December 1998, affects PWS serving at least 10,000 people. Eventually, it is expected that the long-term ESWTR will be applicable to all PWSs regardless of size. This intent is pending the results from the ICR.

Unlike the SWTR, which does not require the source water or drinking water to be monitored for *giardia lamblia cysts* and viruses, the ESWTR does require the PWSs to monitor the influent for these pathogens including *cryptosporidium oocysts* and fecal coliforms. Like the ICR, the monitoring requirements shall be carried out on a monthly basis for 18 consecutive months. This frequency is applicable to large systems (>100,000 population). For smaller systems (but greater than 10,000 population), the frequency of monitoring becomes bi-monthly and only for 12 consecutive months. Furthermore, these smaller systems do not have to monitor their treated water at all. There are some exceptions, however, that allow for early termination of the monitoring duration. Under the ESWTR, a new indicator of pathogen presence may emerge. Although currently E.

Coli has been widely used as that indicator of fecal contamination, viruses coliphage are believed to make the analysis much more simple.

2.1.3 Disinfectant/Disinfection By-Product Rule

The D/DBPR itself, which affects all community water systems that use disinfectants.

The rule was proposed on July 29th 1994 (59 FR 38668) to set Maximum Residual Disinfectant Level Goals (MRDLGs) for chlorine, chloramines and chlorine dioxide. Maximum Contaminant Level Goals (MCLGs) for THMs, HAAs, chloral hydrate, bromate and chlorite would also be set. The rule reduced the Maximum Contaminant Level (MCL) on TTHM and sets new MCL on additional DBPs. It placed a limit on the use of disinfectants and also reduced the level of organic DBP precursors via enhanced coagulation. The D/DBP rule also propose Best Available Technology for Maximum Residual Disinfectant Level (MRDL) and MCL as means of DBP formation control. D/DBP rule sets MCL and MRDL for the following DBPs in 2 stages:

Table 3 Proposed Phased-in of the D/DBP Rule

Parameter	Stage 1*		Stage 2	
	MCL (ppb)	MRDL (ppm)	MCL (ppb)	MRDL (ppm)
THMs	80		40	
HAAs	60		30	
Bromate	10			
Chlorite	1000			
Chlorine		4		4
Chloramines		4		4
Chlorine dioxide		0.8		0.8

* Note: Stage 1 was enacted (Fed. Register. 16 December, 1998, 63(241), 69389-69476).

In addition to proposing the above MRDLGs and MRDLs for disinfectants, the proposed D/DBP rule also set BAT for the control of organic inorganic DBPs which are to be implemented in 2 stages. For stage 1, the BAT for the control of TTHM and THAA shall be GAC10 or enhanced coagulation. Similarly, stage 2 shall require enhance coagulation and GAC 10 or GAC20.

Stage 1 is aimed at maximum control of DBPs utilizing existing processes and technologies. Medium and large PWS systems (>10,000 population) are to comply with the stage 1 requirement by June 30, 2000. Other small systems have a compliance date of January 1, 2002. Stage 2 is expected to set more stringent levels as a result of ICR database.

Note: (a) GAC 10 means Granular Activated Carbon filter beds with an empty-bed contact time (EBCT) of 10 minutes based on average daily flow and a carbon regeneration frequency of 180 days. Similarly, GAC20 implies an EBCT of 20 minutes but with a carbon regeneration frequency of 60 days.

(b) the D/DBP rule at present does not include by-products such as aldehydes, ketones, peroxides, and chlorate. These are expected to be regulated in the future.

ICR, ESWTR and D/DBP Rules are designed to minimize the concentration of disinfectants and disinfection by-products (Lykins *et al*, 1994). With this, at the minimum, the SWTR requires that all-applicable PWSs that have surface water as a source to have enhanced coagulation and filtration treatment. Also SWTR demands that the “c.t” (the product of dosage in mg/L and the contact time in minutes) requirement be met for each disinfectant to ensure antimicrobial contamination. This is where the balancing act is needed because with disinfection comes disinfection by-products (which

is undesirable). Refer to section III for list of DBPs formed from each disinfection process.

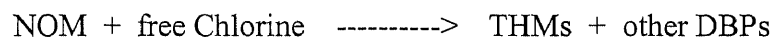
2.2 The Chemistry and Processes of Water Disinfection

The mechanism of disinfection depends largely on the type disinfectant and the type of pathogenic organisms exists in the water (Weber, 1972). It is evidenced that disinfection results from the destruction of cell proteins by inactivation of critical enzyme systems, which are essential to microbiologic life (Lawrence and Hock, 1968). The following are the major disinfectants and their processes:

2.2.1 Chlorine

Chlorination as a disinfection process has been widely employed in the US since 1908. It was reported to be in continuous application in the U.K four years earlier in 1904 (Sawyer and McCarty, 1978).

Chlorination of the water to be treated occurs in the process as described below:

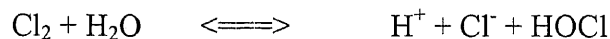


The source of chlorine is obviously from the disinfection process where it is injected for the purpose of oxidizing or inactivating the pathogens.

Other major DBPs include HAAs, HANs, halopicrin, cyanogen chloride, bromate, and chloral hydrate.

The formation of the products in the above equation is a function of chlorine dosage, reaction time, pH, temperature, bromide concentration and the concentration and type of NOM (Weber, 1972; Senesi, 1990).

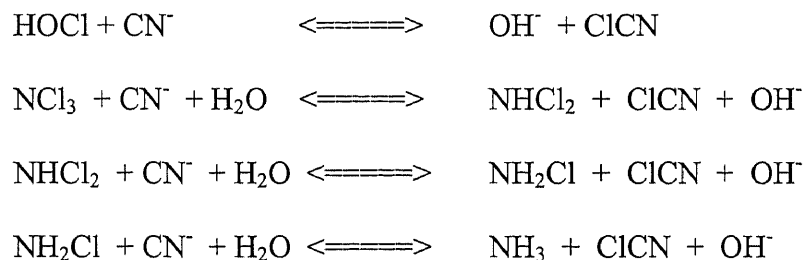
The above equation may be described chemically as following:



Free chlorine may be substituted by its derivatives such as hypochlorous acid or hypochlorite. In fact, these derivatives are used more often than chlorine gas due to the ease of handling and less toxicity. Chlorine is popular as a disinfectant because it is effective at low concentration and is economical (Reynolds and Richards, 1996). The disinfection effectiveness of chlorine is drawn from its ability to oxidize those enzymes of microbial cells that are essential to the cells metabolic processes (Butterfield, 1943). Chlorine is also known for its potent oxidizing power over such metals as iron and manganese.

Chlorine reacts with organic materials to produce chloroform, bromodichloromethane, dibromochloromethane, and bromoform. These are the trihalomethanes DBP of the process.

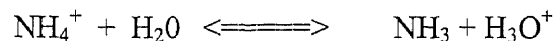
If the water contains cyanide ion, however, cyanogen chloride is produced as a byproduct in accordance with the following reactions (Sawyer and McCarty, 1978):



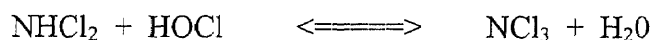
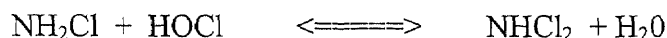
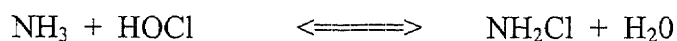
Chlorinated by-products are many. Please refer to section 2.3 for more details.

2.2.2 Chloramine

The chloramination of water, which is another form of water disinfection, takes place in accordance with the following reaction (Sawyer and McCarty, 1978):



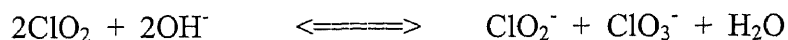
Chloramines are products of chemically mixing of chlorine and ammonia in water solution. Chlorine in the form of hypochlorous acid reacts with ammonia in accordance with the following reactions to yield monochloramine, dichloramine and trichloramine (Sawyer and McCarty, 1978):



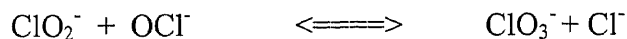
These are DBPs of the chloramination process in addition of chloral hydrate. Chloramines are effective bactericide but are not very effective against viruses. Chloramines provide better disinfection of biofilms in distribution system. The process of chloramination produces less THMs and HAAs as DBPs than the traditional chlorination. Its residual concentration, however, must be higher than that of free chlorine (Chen and Rest, 1996). Chloramination, however, being a weaker oxidant than chlorine also requires significant longer contact times for the same efficacy as in the case of chlorination. The system is physically larger, and consequently more costly. Other disadvantage of utilizing chloramination as disinfection process is that it causes undesirable nitrification in the distribution system.

2.2.3 Chlorine Dioxide

Chlorine dioxide was first introduced as a disinfectant in 1944 at the Niagara Falls (Reynolds and Richards, 1996). This disinfectant was used primarily for tastes and odor controls. Although chlorine dioxide is an unstable gas, which necessitates onsite manufacturing, it is a strong oxidant, which yields very good bactericide characteristics. Chlorine dioxidation has not been used very widely in the US due to the concern of its two DBPs, which are chlorite and chlorate whose health effects are still not very well understood. The problem is worst when the pH of the water is kept high (e.g. above pH 8) for corrosion control purposes. It is in this environment that the formation of chlorite and chlorate are accelerated (Weber, 1972).



Chlorite, which is unstable, reacts with hypochlorite to form chlorate ion, which is more stable in accordance with the following pH-dependent reaction:

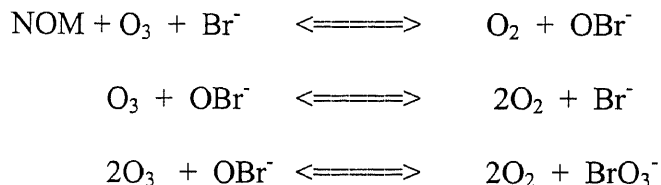


Although chlorine dioxidation disinfects effectively while produces few chlorinated DBPs such as THMs or HAAs, it has its own DBPs of unknown health effects. In addition to the DBP concern, chlorine dioxidation could lead to taste and odor problems in the distribution system (Chen and Rest, 1996). The stability of its residual in the distribution system is also questionable.

2.2.4 Ozone

Yet another popular disinfection process that has been used since 1906 in France is ozonation. In the United States, ozone was slow in being accepted as a powerful

disinfectant. It was not until 1978 that the first plant was commissioned. Ozone, an allotrope, is an excellent oxidizing agent but is unstable with a half-life of about 25 minutes at 20C (Reynolds and Richards, 1996). As chlorine dioxide, it has to be manufactured onsite via ozone generators. The disinfection process occurs in accordance with the following reaction:



These by-products are commonly known as bromate (a B2 carcinogen), brominated acetic acids, bromopicrin, brominated acetonitriles, and bromoform

The process suffers from high capital and operating cost disadvantages and also from the fact that it has no significant residual effect to protect the treated water from possible recontamination. As far as the efficacy of disinfection is concerned, ozonation not only is excellent but also it produces few chlorinated DBPs (Glaze *et al* 1993). Besides disinfection, ozonation provides good taste and odor control, decolorization, oxidation of iron and manganese, and enhancement of TOC removal (Singer, 1990). Because of the instability of its residual, one must rely on other disinfectant (such as chloramination) to guard against recontamination further down-stream in the distribution system. Ozonation has been found to enhance the efficiency of the biological treatment processes as it promotes the microbial activities in the distribution system (Chen and Rest, 1996). Besides having DBPs of its own (ref. section 2.3), ozonation was also observed to increase the concentration of Assimilable Organic Carbon (AOC) which

tends to promote microbial regrowth in the distribution system if it is left uncontrolled (Lykins *et al.* 1994).

2.2.5 Ultra-Violet (UV) Light

Ultra-violet irradiation has been seen in popular use for disinfection. This process of disinfection relies on the exposure of the entire volume of water to the radiation produced by the so-called “germical lamp”. Immersed installations have been found to be more effective than the overhead-radiating-down unit (Loge *et al.*, 1996). The advantages of this process are that it does not introduce any chemical into the water to be treated and that it is cost effective and simple. The associated disadvantage, however, is that it does not have the residual effect. Although the process does not apparently introduce any chemical substance into the water to be treated, it does produce DBPs, at least those that are known to us at the present time (Singer, 1994).

The success of UV disinfection has been found to be dependent on the pretreatment of the water by filtration (Singer, 1994) for low turbidity and low concentration of UV-absorbing substances.

UV - Monochloramine is an attractive combined process except for the disinfection of *giardia* and *cryptosporidium cysts*.

2.2.6 Titanium Dioxide Photocatalysis (TiO₂/UV)

This disinfection process is effective against viruses. It produces no THM DBPs (Okun, 1994). The mechanism of disinfecting by photocatalysis was described as following (Richardson *et al.*, 1994):

“When TiO_2 is illuminated with at wavelengths of light less than 388nm, an electron is excited from the valence band to the conduction band, leaving an electronic vacancy called a hole ($\text{h}\nu\text{b}^+$) in the valence band. This hole then reacts with OH^- ions in water and H_2O molecules to produce hydroxyl radicals (OH), one of the most powerful oxidizing agent known. This photocatalytic oxidation process has been shown to successfully degrade a wide variety of organic contaminants, including trichloroethylene, THMs, pesticides, PCBs, and PAHs into non-toxic compounds such as simple mineral acids, carbon dioxide, and water. As a result, if TiO_2 photocatalysis is used to treat drinking water, it has the potential to degrade raw water contaminants as well as DBPs as they are being formed. In addition, sunlight (which starts at a wavelength of 300nm) can be used as a light source, which could allow this method to be a potentially inexpensive technique for degrading organic contaminants and disinfecting drinking water”.

The disinfection process, as expected, is not without DBPs. It has been found that when the process used with ultrafiltration treatment, the only DBP produced is 3-methyl-2,4-hexanedione. Obviously when treated with secondary chlorination for residual effect, other chlorinated and brominated DBPs will result in addition to dihydro-4,5-dichloro-2(3H) furanone (Okun, 1994).

2.3 The formation of Disinfection By-Products

Depending on the process of disinfection, different DBPs are formed as discussed in the previous section. Table 4 presents a summary of these disinfection by-products.

Table 4 A Tabulation of Different Disinfection Processes and Their Resultant DBPs (Marhaba and Washington, 1998)

Disinfection Process	Disinfection By-Products
Chlorination	Trihalomethanes, Haloacetic acids, Haloacetonitriles
Chloramination	Chloral hydrate
Chlorine Dioxidation	Chlorate, chlorite, chlorophenols, quinones
Ozonation	Aldehydes, carboxylic acids, quinones, peroxides, Bromates, Brominated products
Titanium Dioxide	3-methyl-2,4-hexanedione, dihydro-4,5-dichloro-2(3H)
Photocatalysis	Furanone

It is convenient from the regulatory and industry standpoint to categorize the related DBPs. The following table presents such grouping:

Table 5 DBP Grouping and the Associated DBP Constituents (Marhaba and Washington, 1998)

DBP Group	DBPs
THMs	Chloroform (also known as Trichloromethane) Bromodichloromethane Dibromochloromethane Bromoform (also known as tribromomethane)
HAAs	Monochloroacetic acid Dichloroacetic acid Trichloroacetic acid Monobromoacetic acid Dibromoacetic acid Tribromoacetic acid Bromochloroacetic acid Bromodichloroacetic acid Dibromochloroacetic acid
HANs	Dichloroacetoneitriles Trichloroacetoneitriles Dibromoacetoneitriles Tribromoacetoneitriles Bromochloroacetoneitriles
Cyanogen Halides	Cyanogen chloride Cyanogen bromide
Halopicrins	Chloropicrin Bromopicrin
Haloketones	
Haloaldehydes	
Halophenols	
MX	Furanone

The formation of the above DBPs is strongly influenced by pH, contact time, seasonal temperature, nature of NOM, concentration of NOM, chlorine dose and residual, and bromide concentration.

DBP formation potential is found to be directly proportional to all the above parameters except for the pH, which means when the pH is raised, less DBP is formed.

The reverse is true when the pH is lowered.

2.4 Health Risks Associated with each DBP

It has been known that chlorine does not cause cancer. By-products from chlorination do. It is also true for other disinfectants as well.

Generally, Disinfection By-products, according to the EPA in its summary for the ICR final rule, may have adverse human health effects, including cancer, liver and kidney damage, heart and neurological effects. The health effects could be extended to unborn children as well. Tap water and miscarriages have been the concerns among pregnant women as reflected by the current court cases in California and North Carolina (Waternews, 1999; Medscape, 1998).

Chloroform was specifically declared as a carcinogen by the National Cancer Institute (1976) which resulted with the regulation of TTHM at a then-MCL of 0.1 mg/l for PWS serving a population of greater than 10,000. The trend is expected to be getting stricter with MCL in the range of 10 to 25 ppb can be expected. It should be noted that the MCL is imposed on the TTHM (the sum of all the derived forms of THMs and not on the individual THM such as chloroform, dichlorobromoform, dibromochloroform or bromoform.

As for other classes of DBPs, the following health effects have been documented (Singer, 1994):

- Dichloroacetic acid is more carcinogenic than THM
- Furanone is extremely mutagenic even at very low concentration of 0.05 ppb
- Bromate from ozonation is a class B2 carcinogen that has a MCL of 10ppb.
- Among the non-brominated DBPs as a result of ozonation, aldehydes appear to be of the greatest health concerns

Chlorite and chlorate ions as a result of chlorine dioxidation cause hepatotoxicity in animals. They also have been observed to produce hemolytic anemia, which can cause damage to red-blood cell membrane (Hautman *et al* 1992).

2.5 Related Prior Researches

2.5.1 Fluorescence spectroscopy

Chubarov *et al* (1994) conducted a study of natural water using laser fluorescence spectroscopy for the diagnostics of pollutants such as petroleum hydrocarbon, humic substances and proteins in the open sea. It was found in this investigation that excitation done at lower wavelength would yield better and more informative data. Lower wavelength excitation means higher energy bombardment of the sample. Different peaks occur due to different atomic structures, i.e, for hydrocarbon, peaks around (290nm - 308nm) correspond to 1 or 2 ring aromatics while peaks around (360nm - 385nm) are caused by 3 or 4 ring aromatic structures. The study also found that fluorescence intensity is strongly dependent on concentration at a given excitation wavelength. The authors documented a minimum detectable value of 0.5 ppb using the fluorescence technique with an analysis time of not more than 15 minutes.

About the same time, Orlov *et al* (1995) conducted research focusing on the technical challenge of rapid diagnosis of organic pollution of water and wastewater. 2-D Spectral Fluorescence Signatures (SFS) were proven to be that promising method that could face up to the challenge. This work dealt primarily with polluted water in the open sea with dissolved organic matter as a background. 13 SFS of different pollutants and 6 SFS of different DOM were used to build a neural networks-based system showing the

potential for a solution toward the problem of detection, identification, and concentration measurement of water pollution. It was suggested that SFS could be developed as rapid tool to monitor the water quality environment including detection, identification and quantification of the concentration of organic pollution. The study found that SFS method as used in its study was not as accurate and sensitive as other method for pollutant identification. What makes SFS attractive, however, is that it affords the possibility of recognizing complex mixtures of pollutants, and that a wide range of pollutants that can be classified. SFS method was found to be attractive also because of its non-requirement of sample preparation.

Recognizing that decomposing complex conglomerate, such as organic matter in water and wastewater, into their chemical ingredients for analysis is an impossible task, Babichenko *et al* (1995) suggested an alternative approach which treats the object as an integral spectroscopic sample to be characterized by SFS. SFS could either be the fluorescence spectra obtained at the most effective excitation wavelength or the sum total of the emission spectra of an object at different excitations. For Dissolved Organic Matter (DOM), the peak occurs at an excitation of about 325nm. Chl. a at 425nm, Chl. b at 480nm and Phycoerythrin at 540nm. SFS method was used in an in-flow mode to demonstrate the feasibility of an on-line fluorescent technique to diagnose the water environmental that was contaminated with crude oils, lubricants, fuels, residual oils, shale oils, phenols and their derivatives, fulvic acids and aromatic amino acids. Confirmation was made that the intensity varied proportionately with the concentration and that the location of the peak is stationary irrespective of the concentration of the pollutant. It was found, in case of this study, that SFS is less sensitive than other contact and preparative

methods. It is, however, a more convenient and expeditious analytical tool. SFS as an analytical tool started to be used at the New Jersey Institute of Technology in 1997 with the characterization of humic substances which were derived from soil, peat and water (Washington, 1998).

Senesi *et al* (1989) conducted fluorescent analyses of eleven fulvic acid (FA) and humic acid (HA) standards. These standards were extracted from different aquatic and terrestrial origins that were collected by the International Humic Substances Society. It was found that the emission spectra peaks at 510nm for soil, peat and leonardite HA, 471nm for river and nordic aquatic HA. For all FAs, the peaks are in the range of 457nm to 465nm. Excitation spectra showed better resolution than that of the emission spectra. With better resolution, terrestrial HAs do show double peaks at 450nm and 467nm and a less intense peak at 390nm. For aquatic HAs and FAs, main peaks are found at around 388 to 395nm with a minor peaks at 440 to 467nm. The analysis of HAs and FAs was expanded a step further by Kochar (1999) in which not only these substances were characterized by SFS, their concentrations were also correlated with the formation of potential of the various classes of DBPs.

Another marine water research utilizing fluorescence spectroscopy was conducted by Sierra *et al* (1994). The study concluded that fluorescence signature can be used to differentiate water masses at appropriate excitation wavelength, i.e., 313nm. For natural waters, it was found that fluorescence peaks were found in the 350-550 nm range depending on the excitation wavelengths. Pure compound, however, was reported to have peak at a fixed location regardless of the excitation wavelength.

The use of fluorescence spectroscopy was documented in a research by Senesi (1990) to investigate the molecular and quantitative aspects of the chemistry of fulvic acid and its interactions with metal ions and organic chemicals. This study documented peaks of an array of fulvic acids, which again confirmed the fact that terrestrial soil-derived FAs normally exhibit dual peaks while aquatic FAs normally show single peaks. Fluorescence properties such as intensity were found to be a strong function of (1) molecular weight, (2) concentration, (3) pH, and (4) temperature. The relationship between intensity and each of the above parameters, except for concentration, is inversely proportional. An important finding from this research also was that the presence of heavy metal has a quenching effect on the fluorescence of humic substances.

Water was fractionated both by tangential ultrafiltration and resin and then subject to a comparison analysis. Belin *et al* (1993) conducted this analysis utilizing fluorescence spectroscopy, which showed that the two methods of fractionation and isolation were equally effective. It was shown that “the fluorescence technique could be applied in parallel with dissolved organic carbon (DOC) determination to estimate the relative contribution of the different families of the DOM in natural waters and to detect their chemical modifications.

One of the first papers that documented some correlation between fluorescence and HPLC data to yield prediction on the concentration phytoplankton pigments was accomplished by Kaitals *et al*. Research approach was such that a basic SFS catalogue of the most important phytoplankton species was created. Data generated by fluorescence and high Performance Liquid Chromatography (HPLC) were then matched with the basic catalogue of data for comparative analysis. Research results showed good potential for

rapid remote analysis of pigment composition in mixed phytoplankton community using fluorescent diagnostics.

Huang and Smith (1984) developed a spectrophotometric method for the determination of trihalomethanes in drinking water. This colorimetric method was based on the fact that when a halogen compound is heated with sodium hydroxide and pyridine the solution can be characterized by its red color. A visible spectrophotometer was used to measure the absorbances of the THM-pyridine complexes. As a result, a straight-line calibration curves were developed by plotting the absorbances of the solutions against the THM concentrations. The method, although less sensitive and less specific than the Gas Chromatography with Electron Capture Detection (GC/ECD) method, was found to be useful due to its simplicity, screening ability and cost economy.

2.5.2 Disinfection By-Product Formation Potential

More closely related to this research as far as the use of the fluorescence spectroscopy technique on NOM fractions and characterization is the report by Owen *et al* (1993) in which NOM was fractionated by resin adsorption and by ultrafiltration membrane. The humic character fractionation led to the isolation of only two fractions, however, which are humic and nonhumic in nature. Each fraction was subjected to DOC, ultraviolet (UV), fluorescent analyses and formation potential (FP) test. Fluorescence intensity at the most sensitive emission wavelength was the parameter that was reported. To take it a step further from two fractions and 96-hour FP procedure of the preceding report, another study (Korshin *et al*, 1997) was done which employed the resin adsorption technique to fractionate DOM into six different finite fractions which are hydrophobic base, acid,

neutral and hydrophilic base, acid and neutral fractions. Each fraction was subjected to a 168-hour FP test in the reaction with chlorine for the analysis of total organo-halides (TOX). TOX FP, and not the individual class of DBPs, was the subject of the study. Characterization of fractions was done by UV at 254nm and NMR spectroscopy. It was suggested that DBP precursors could be removed by adsorption onto iron-oxide-coated sand (IOCS).

2.5.3 DOM Fractionation

Concerning the fractionation of DOM by resin adsorption, the procedure has been used and proven to be effective by Leenheer (1981), Day *et al* (1991) and Korshin *et al* (1997). These researchers fractionated samples of DOM into 6 different fractions, which are hydrophobic base, hydrophobic acid, hydrophobic neutral, hydrophilic base, hydrophilic acid and hydrophilic neutral. Other resin adsorption procedures were also used by Thurman and Malcolm (1981), Croue *et al* (1993) and Bose *et al* (1994). These procedures focused more on the isolation of the humic substance or hydrophobic material than the counter part nonhumic substance or hydrophilic material.

It should be noted that neither the fluorescence nor excitation of each fundamental fraction of DOM, chlorinated or not, has been given in literature.

2.6 The Characterization of NOM

NOM, being vegetative derivatives, soil corrosion, animal biodegradation and other miscellaneous debris, has been characterized as consisting of two principal substances which are humic and nonhumic (Owen *et al*, 1995). Humic substance and hydrophobic

substance have been used interchangeably in literature. The same is true for nonhumic substance and hydrophilic substance. To characterize the NOM, there are principally three approaches (Krasner *et al*, 1996) that have been used. They are

- Nonperturbing approach. Samples remain intact during the analyses. Under this approach, the morphology of samples can also be observed using Transmission Electron Microscopy (TEM) whose samples are mixed with melanine resin in a viscous state.
- Isolation-fractionation approach. This approach is to characterize the NOM of each fraction and determine its contribution to the DBP FP. Among the techniques are precipitation, ultrafiltration (Newcombe, 1997), solvent extraction, freeze-drying, macroporous resin adsorption (Thurman and Malcolm, 1981), non-adsorption method, and Reverse Osmosis (Crum *et al*, 1996). Analyses are done by Py-GC-MS through which the DBP FP, the elemental compositions and amino acids contents can be measured.
- Calculations approach. This approach provides the most probable values for aliphatic carbon, aromatic carbon and “excess” carbon in a sample of NOM

With the above approaches, NOM can be characterized as following (Owen *et al*, 1995):

2.6.1 Humic Substance

- Hydrophobic in nature which constitutes about 50 to 65% of DOC. This fraction is further subdivided into 10% hydrophobic neutral fraction and 90% hydrophobic acid fraction, which are known as humic and fulvic acids (Thurman and Malcolm, 1981; Owen *et al* 1995)

- Adsorbed onto XAD-8 amberlite resin in the fractionation procedure (Leenheer, 1981; Thurman and Malcolm, 1981).
- Aromatic in molecular structure (Collins *et al*, 1986).
- Characterized by such surrogates as DOC, UV absorbance, Trihalomethane Formation Potential, Apparent Molecular Weight (AMW), acidic functional group such as carboxylic and phenolic acid (Collins *et al*, 1986).
- Reactive to chlorination to form DBPs (Rook, 1974).
- Non-volatile and polar (NJDEP, 1983).
- Resistant to microbial degradation (Amin *et al*, 1996)
- Able to complex with metal to re-pollute the water (Amin *et al*, 1996).
- Made up of ketonic, carbonyl, aromatic and phenolic compounds. When these precursors are further broken off, chlorinated activity is lessened and DBP formation was found to decrease (Eggins *et al*, 1997)

2.6.2 Nonhumic Substance

- Hydrophilic constitutes about 20 to 30% of DOC. Nonhumic substance consists of proteins, amino acids and carbohydrates (Owen *et al.*, 1993).
- More abundant in oxygen content than its counterpart hydrophobic (Owen *et al.*, 1993).
- Is hydrophilic in nature (Amy, 1993).
- Adsorbed on XAD-4 amberlite resin (Leenheer, 1981)
- Characterized by BDOC (Owen *et al.*, 1993)

- As reactive to chlorination to form DBPs as its counterpart humic substance (Owen *et al.*, 1995)
- Non-volatile and nonpolar (NJDEP, 1983).
- Made up of carbohydrates, uronic acids and hydroxy acids (Collins *et al.*, 1986).

2.7 Treatabilities Regarding DBP Precursor Removal

Among the treatment that are widely acceptable for DBP precursor removal are Coagulation, GAC and Membrane Separation (Jacangelo *et al.*, 1995). Coagulation is the most widely used and economical. Coagulation effectiveness is found to be a function of four factors (Najm *et al.*, 1994): NOM concentration, NOM type, coagulant dosage, and coagulant pH.

The first two factors are boundary value conditions for a particular water source and are hence non-manipulative. Optimizing the coagulation process then involves the control of pH level and coagulant dosage. In fact, coagulation pH was found to be the determining factor for maximum DOM removal (Crozes *et al.*, 1995) and DOM fractions' removal (Pipada, 1999).

Different treatment processes are applicable to different DOM substances as shown in the following table.

Table 6 Suggested Treatment Processes for Different Types of NOM Fractions (Marhaba and Washington, 1998; Amy, 1993)

For Fraction of the following type	Suggested treatment process
Humic substance	Coagulation, adsorption, membranes
Nonhumic substance	Membranes, biodegradation
Higher MW	Coagulation, membrane
Medium MW	Adsorption, membrane (UF or NF)
Lower MW	Membrane (NF), Ozone-induced biodeg.

Regardless of the process, higher pH and alkalinity have documented to be the obstacles of NOM removal.

In addition to these traditional DBP precursor methods, removal by photodegradation is becoming more popular. Amiri *et al* (1997) found the UV-vis/ferrioxalate/H₂O₂ to be a very efficient process in removing organic compounds in contaminated water. The problem has been and continues to be one that we do not know what kind of DBPs will result from a particular new disinfection process or disinfectant and to what extent their toxicity will have on human health. This research will focus primarily on chlorine as the disinfectant.

2.8 Correlations Regarding the DBP Formation Potential

The concentration of THMs formed during chlorination has been correlated with various nonspecific parameters such as raw-water DOC, UV absorbance, and chlorine demand (Bruchet *et al*, 1990), which may not be entirely appropriate. Py-GC-MS was proven by as a technique to determine the relationship between trihalomethane formation potential (THM FP) and the organic content of the water. It was reported (Amy, 1993) that while correlations among DOC, UVA and Fluorescence are generally good for raw as well treated waters, correlations between THM FP and other surrogates are generally not good, especially when the waters are of multiple sources such as unreactive high-DOC or reactive low-DOC.

THM Correlations:

The following correlations were developed at standard conditions of pH and temperature unless otherwise noted:

- $$\text{TTHM} = 0.00325(\text{UVABS.TOC})^{0.378} \times (\text{CLDOSE})^{0.517} \times (\text{RXNTM})^{0.252} \times (\text{TEMP})^{0.985} \times (\text{pH}-2.6)^{0.640} (\text{BR}+1)^{0.0536} \quad (\text{Amy et al. 1987})$$

Note: 8hrs < RXNTM < 24 hrs

UVABS = UV absorbance

TOC = Total Organic Carbon

CLDOSE = Chlorine dosage

RXNTM = Reaction time

TEMP = Temperature

BR = Bromide concentration

- $$\begin{aligned} \text{TTHM} = & -3.34 + 0.317(\text{UVABS.TOC}) + 0.968\exp^{0.0457(\text{TEMP})} + 0.0101(\text{CLDOSE})^{1.22} \\ & + 0.201(\text{BR})^{1.70} + 1.32(\text{RXNTM})^{0.217} + 0.0926(\text{pH}-2.6) \end{aligned}$$

(Amy et al. 1987)

Note: RXNTM < 8hrs

- $$\begin{aligned} \text{TTHM} = & -11.0 + 0.618(\text{UAVABS.TOC}) + 0.968\exp^{0.124(\text{TEMP})} + \\ & 0.0266(\text{CLDOSE})^{1.33} + 0.795(\text{BR})^{1.77} + 5.66(\text{RXNTM})^{0.0943} + 0.285(\text{pH}-2.6) \end{aligned}$$

(Amy et al 1987)

Note: RXNTM > 24hrs

- **THM FP**, ug/L = $54.0 [± 4.8] \times \text{TOC mg/L} + 46.6 [± 76.5]$

With a correlation coefficient $R = 0.828$

(Singer and Chang 1989)

- **THM FP**, ug/L = $2118 [± 178] \times \text{UV} + 101 [± 74]$ with $R = 0.89$

(Singer and Chang 1989)

Good correlations exist between Simulated Distribution System THM (SDSTHM) and THM FP in case of coagulation (Amy, 1993). This is not so in case of ozonation. Regardless of the treatment, however, there is no acceptable correlation between Haloacetic acid formation potentials (HAA FPs) and THM FPs or between THM FP and chlorine demand.

“Excellent correlations have been obtained between TOC and THM FP for a single water... However, when waters from different sources are included, the correlations are sometimes not as good. This is because waters from different sources tend to have different specific THM yields, i.e., THM FP:TOC as determined by their particular sourcewater characteristics.” (Reckhow and Singer, 1990)

There are no correlations reported between DBP precursors on the fractional levels and Spectroscopic parameters.

CHAPTER 3

OBJECTIVES

Although the topic of DBP formation potential and DBP precursor removal have been studied by many researchers since Rooks (1974), the efficacy of methods that have been developed to date has been handicapped by the notion that DBP precursors can be, and have been, represented by the surrogate parameter TOC, which is aggregate in nature. Although all DBP precursors contain carbon, not all carbon-containing substances are DBP precursors, however. The question of what really is, or are, responsible for the formation of DBPs must be addressed and answered. The time for the so-called guilty by association must end. Using the aggregate TOC, however, has not revealed the identification of the problematic precursor leading to the formation of THMs, HANs or HAAs. No optimization of DBP precursor removal could be done without this critical information. Finally, current analytical work leading to the identification and quantification takes far too long to keep track of the fast-changing characteristics of the sourcewaters. Normal analytical work at present is about 10 days to 2 weeks employing fractionation techniques, formation potential procedure, liquid-liquid extraction for GC analytical procedure, etc.

To improve upon these shortfalls, this investigation has the following objectives:

3.1 Development of SFS Method for Rapid Identification of Target THMs and HAAs Precursors

To accomplish this, samples must be isolated into finite fractions. Develop a method to scan the fractions and a system for data management. Data for each fraction are to be catalogued and analyzed to develop spectral identification criteria to distinguish one fraction from another.

3.2 Development of a Gas-Chromatography (GC) Generated DBP FP Database

Conduct formation potential test on each fraction to study the chlorinated reactivity of each fraction. Conclusions are to be made as to whether which of the fraction is or is not chlorinated DBP with respect to THMs and HAAs. For each concentration of the fractionated precursors, estimate the formation potential. Formation potential data are to be assembled into a DBP FP database.

3.3 Development of a Computer-Based Predictive Tool to Integrate SFS Data in the Computation of DBP FP

To develop a rapid tool to identify and calculate the DBP precursors and their associated FP, it is necessary to write 2 computer codes with the capability to work in a complementary fashion. One code, called the SFS4IDN, will read raw data as a result of a fluorescent scan. The end result to be produced is the concentration of each precursor. Another code, called GC4DBPFP, will accept as input the results from the previous code to ultimately produce the FP of each fraction's concentration.

The codes are to have graphical user interface (GUI) features and to run from a desktop with Visual Basic compiler.

The ultimate goal is to recommend the use of this study and toolkit for the work toward optimizing the chlorinated DBP precursors removal in water treatment in a rapid (less than 1-hour time) and cost effective fashion with reasonable accuracy and precision.

CHAPTER 4

MATERIALS AND METHODS

4.1 Participating Water Treatment Plants

Water samples were collected from the following three participating water treatment plants: The Raritan/Millstone (R/M) and the Canal Road (CR) surface water treatment plants of Elizabethtown Water Company (Westfield, NJ) are located in central New Jersey and have an average combined process flow of about 570,000 m³/day. Sources of water for both plants are the Raritan and Millstone rivers, augmented by Spruce Run and Round Valley reservoirs, and the Delaware and Raritan Canal. The CR plant utilizes preozonation, coagulation, sedimentation, intermediate ozonation, and multimedia filtration with post chloramination, whereas the R/M plant utilizes conventional treatment with intermediate chlorination and post-chloramination as the disinfection process as shown in Figure 4 and 5, respectively. It's important to note that the GAC-containing filter of the CR plant is also a biofiltration in its functionality. In fact, the assimilable organic carbon (or AOC ref. *Standard Methods* 9217B) which is the easily biodegradable part of the DOC of the water sample was observed to be reduced (in the range from 33% to 60%) across the filter. This reduction comes after an expected increase in this parameter due to ozonation (both from the preozonation and intermediate ozonation stages).

The following protocol as shown in figure 3 was implemented throughout this research. All terminologies and acronyms will be provided in the appropriate context of the dissertation.

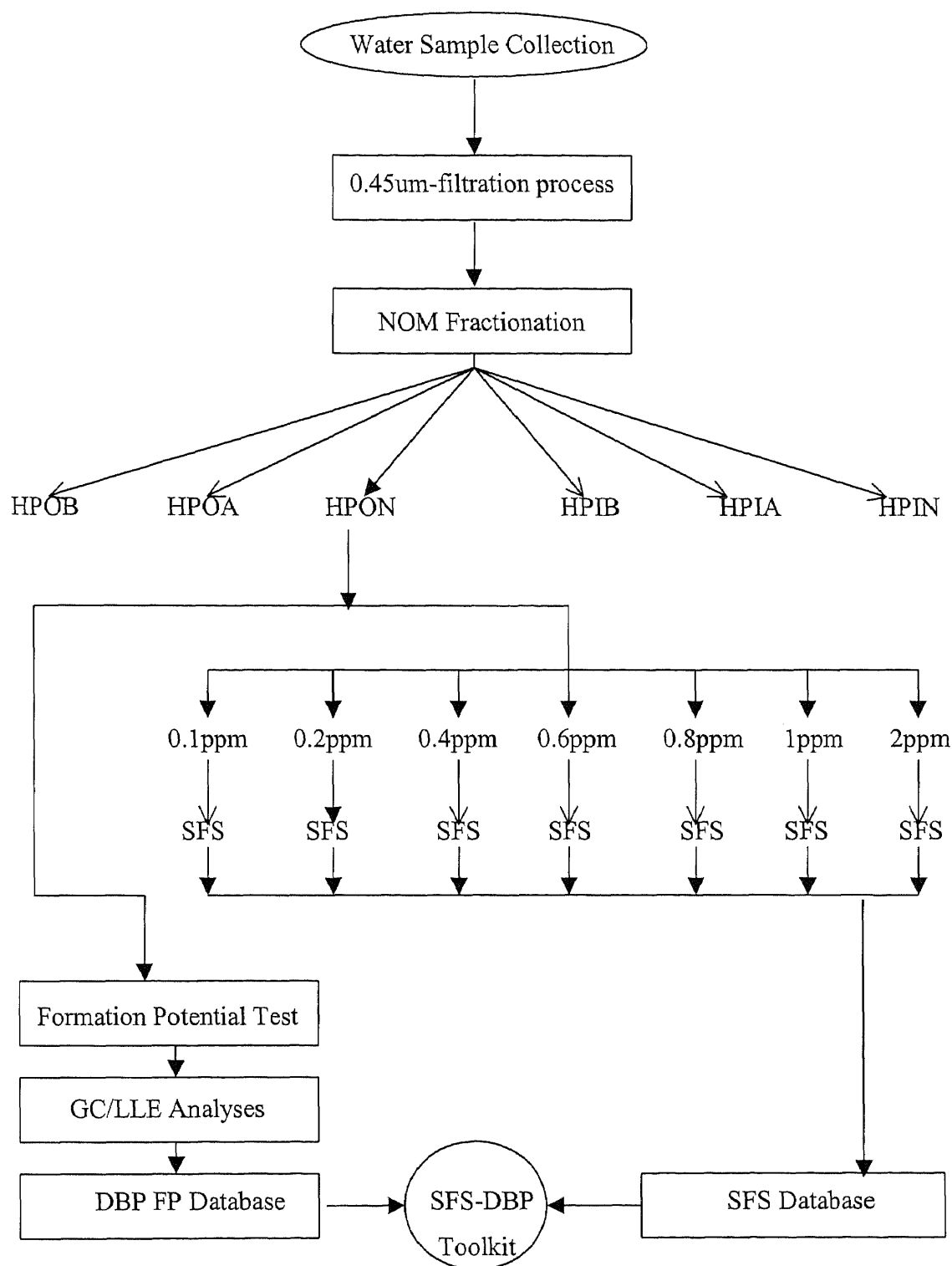


Figure 3 Research Protocol

The Passaic Valley (PV) surface water treatment plant of Passaic Valley Water Commission (Little Falls, NJ) is located in northern New Jersey and has an average process flow of about 210,000 m³/day. Source of water is the Passaic River. The PV plant utilizes pre-chlorination, coagulation, sedimentation, post-chlorination, and anthracite over-sand filtration, as shown in Figure 6.

Table 7 contains unit process descriptions and water quality data of the three participating water treatment plants. Sampling locations for this study were collocated with the Information Collection Rule points in the treatment train and are illustrated in figure 4, 5 and 6.

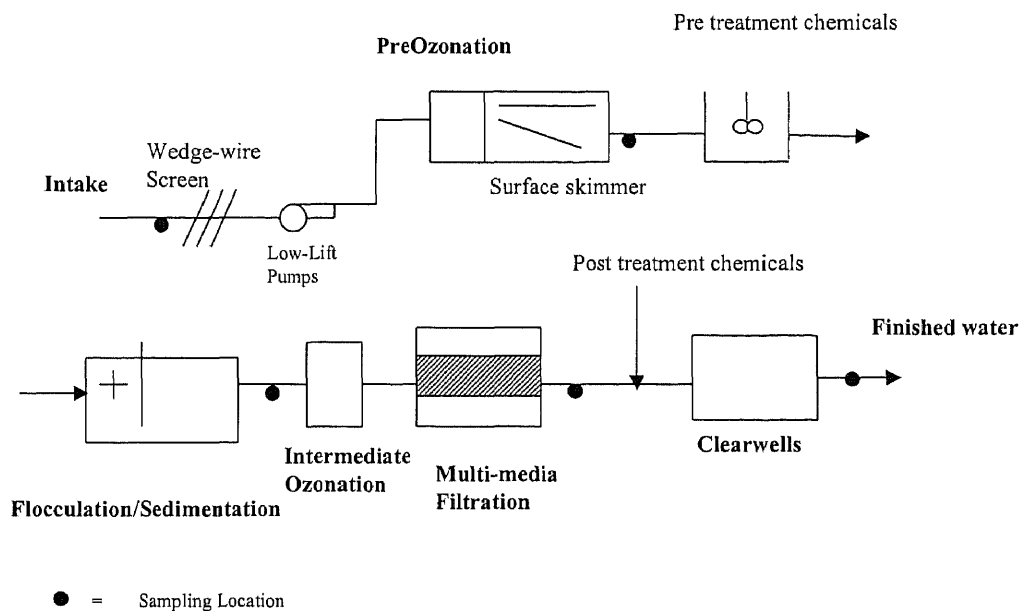


Figure 4 Canal Road (CR) Water Treatment Plant

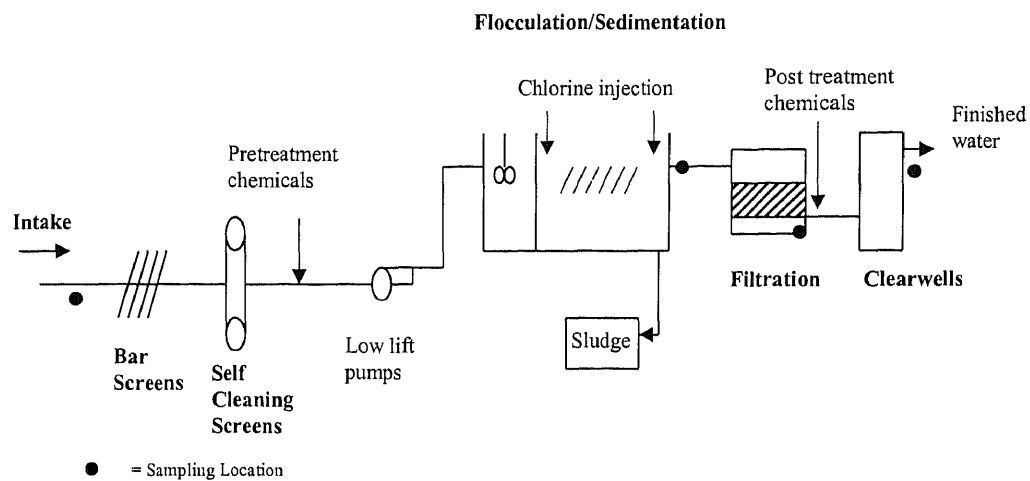
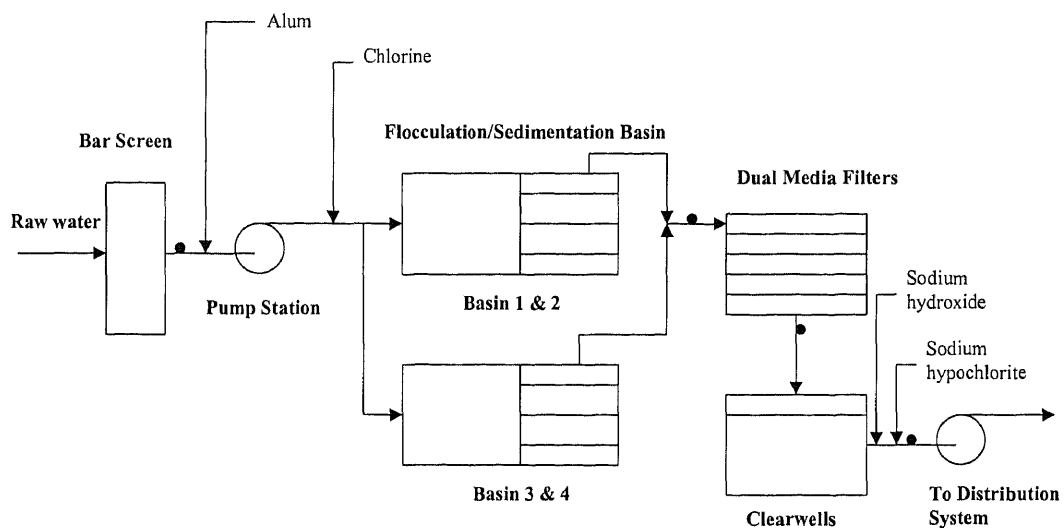


Figure 5 Raritan Millstone (RM) Water Treatment Plant



- = denotes sampling point

Figure 6 Passaic Valley (PV) Water Treatment Plant

Table 7 General Description of the Participating Water Treatment Plants and the Associated Water Quality

Unit Process	Canal Road WTP	Raritan-Millstone WTP	Passaic Valley WTP
Plant Flow	90,000 m ³ /day	380,000 m ³ /day	210,000 m ³ /day
Pre-Ozone Contact time Dosage	9.25 min 0.25 mg/l	N/A	N/A
Pre-Treatment Chemicals & Dosages	Liquid alum (23 mg/l)	Liquid alum (27 mg/l) Sulfuric acid (20 mg/l) KMnO ₄	Liquid alum (20 – 70 mg/L) Chlorine (4.7 mg/L)
pH (coagulation chamber)	6	6	6
Sedimentation Type	Conventional	Tube settler	Conventional
Intermediate Ozone Contact time Dosage	30 min. 0.50 mg/l	N/A	N/A
Filter media	Multi-media (GAC, sand, ilmenite) and dual-media (GAC, sand)	Anthracite, sand, garnet	Dual-media (20-inch anthracite over 10-inch sand)
Post-Treatment Chemicals	Sodium hypochlorite (1.7 mg/l) Aqua ammonia (0.37 mg/l) Sodium hydroxide (8.7 mg/l) Zinc orthophosphate (0.50 mg/l)	Sodium hypochlorite (2.1 mg/l) Aqua ammonia (0.36 mg/l) Lime (12 mg/l) Zinc orthophosphate (0.44 mg/l)	Sodium hypochlorite (1.0 mg/L) Sodium hydroxide (15.1 mg/L)
Influent DOC (mg/l)	4.00	4.00	4.6
Ozone-DOC ratio	0.06 – 0.13	NA	N/A
Bromide (mg/l)	0.03	0.03	<0.0046
Influent Turbidity (NTU)	11	11	4.7
Influent pH	7.2	7.2	7.5
Alkalinity (mg/l as CaCO ₃)	28	28	46
Hardness (mg/l as CaCO ₃)	52	52	56

All samples were personally collected, secured and transported to ensure consistent in quality control. In the lab, samples were refrigerated at 4°C and analyzed within the specified holding time. Milli-Q water was used for all dilutions, solution preparation and final glassware washing. All chromatography columns were of borosilicate glass (Kontes, Vineland, NJ) with 20-micron polyethylene bed support disc. Isolated fractions (70-250ml) were also kept refrigerated at 4°C in quality-assured amber glass bottles.

4.2 DOM Isolation & Fractionation

Dissolved organic matter (DOM) fractionation was carried out using a modified resin isolation/fractionation procedure similar to the one described by Leenheer (1981). The modified method is described by Marhaba *et al*, 1999. The following is a summary of the fractionation procedure that was implemented (ref. figure 7-11)

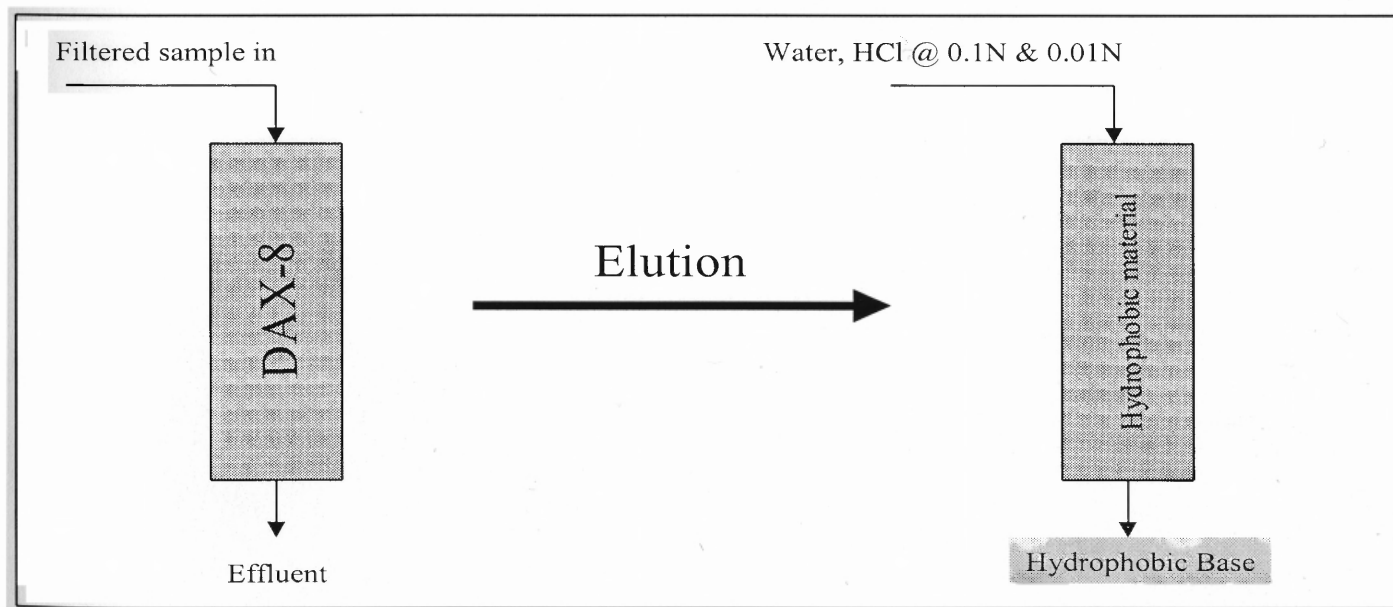


Figure 7 Isolation of the Hydrophobic Base Fraction

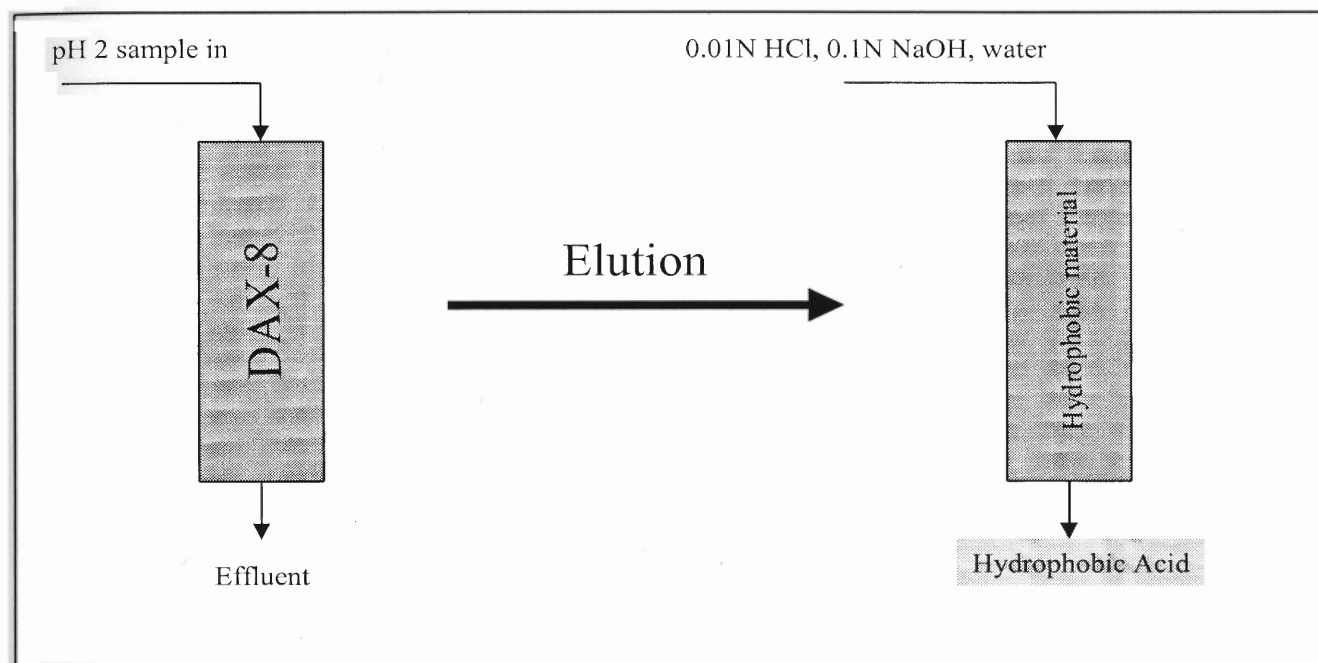


Figure 8 Isolation of the Hydrophobic Acid Fraction

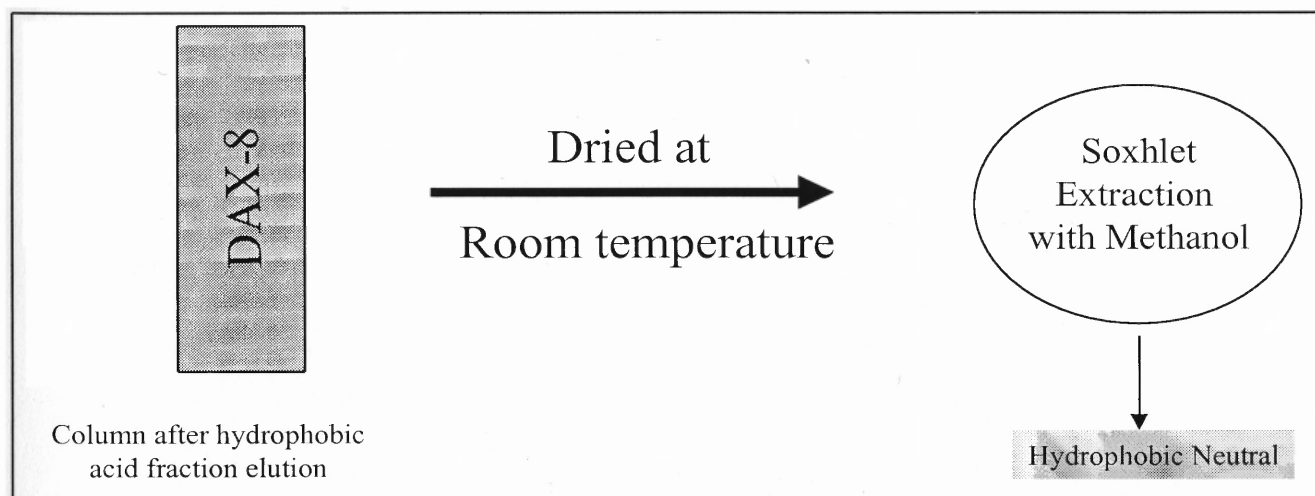


Figure 9 Isolation of the Hydrophobic Neutral Fraction

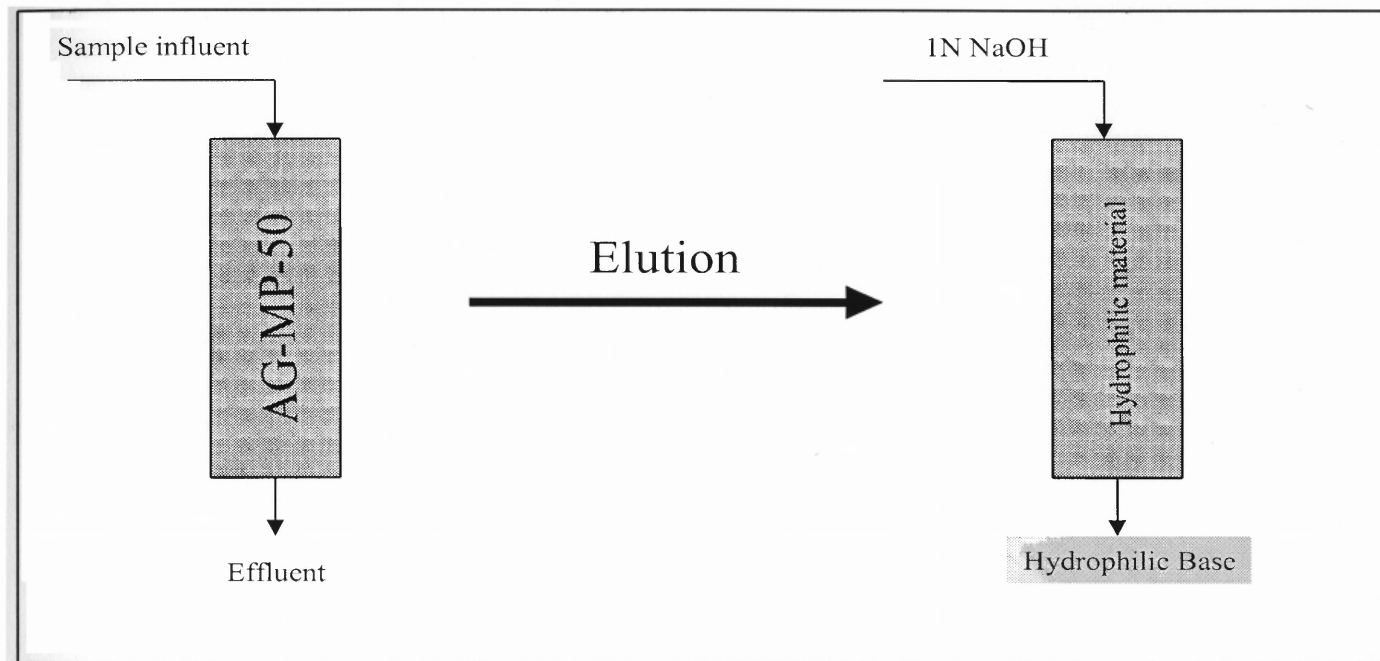


Figure 10 Isolation of the Hydrophilic Base Fraction

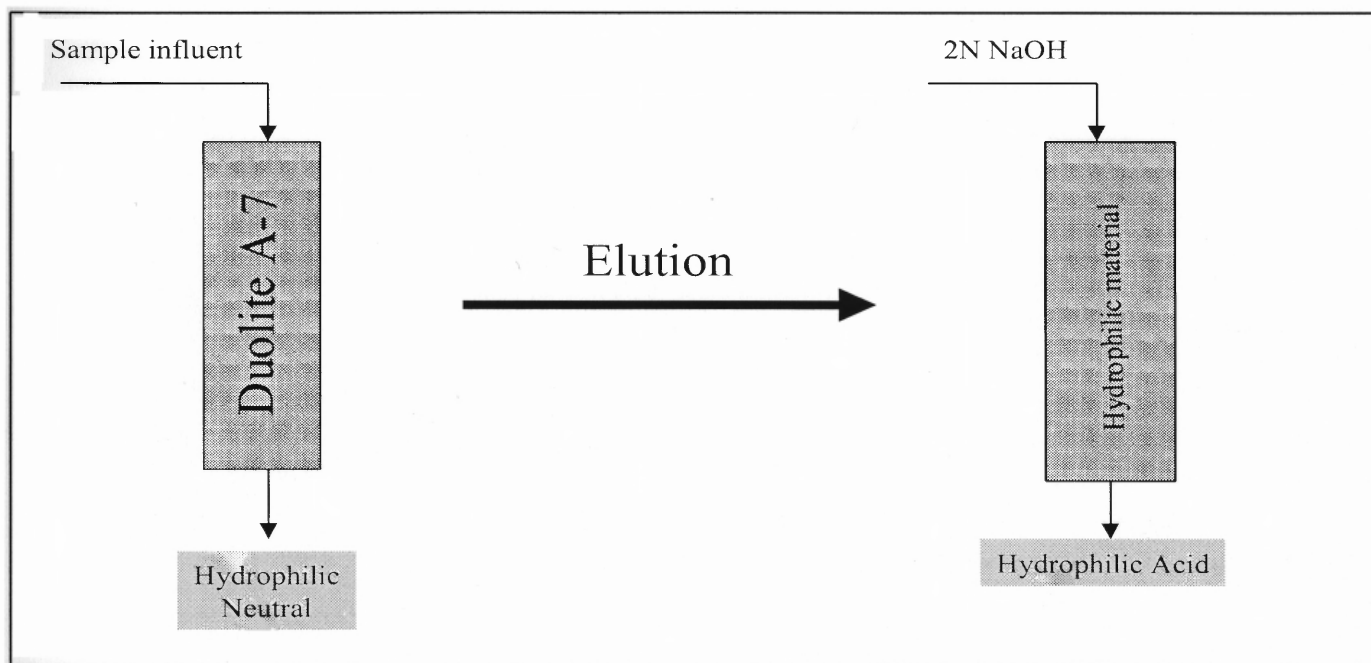


Figure 11 Isolation of the Hydrophilic Acid and Neutral Fraction

Original samples, each of 9-liter volume, were collected from the plant locations shown in Figure 4, 5, and 6. All samples were filtered through a 0.45-um cellulose filter to transform the raw water samples into Dissolved Organic Matter (DOM) water samples. This intermediate filtration step is necessary so that only DOC and not TOC is considered. It is presumed the matter that is not be dissolved can be, one way or another, settled out or screened out of the water before it can come into contact with chlorine. Amberlite resin DAX-8, a macroporous methylmethacrylate copolymer (Supelco, Bellefonte, PA), AG-MP-50, a strong acid, sulfonated, polystyrene macroporous resin (BioRad, Hercules, CA) and Duolite A7, a weak base, phenol-formaldehyde condensation macroporous resin (Supelco, Bellefonte, PA) were all purified by soxhlet extraction prior to being used in the process (reference figure B1, B2, B3). Filtered samples were pumped through the DAX-8 column (figure 7). The retained, hydrophobic base was then eluted by a sequential flow of 0.1N and 0.01N HCl. The DAX-8 column (figure 8) effluent was then acidified with 6N HCl (dropwise) to pH 2 to be recycled through the DAX-8 column. The retained, hydrophobic acid was then eluted with 0.1N NaOH. The DAX-8 resin was then dried for 15-24 hours at room temperature prior to being soxhlet-extracted with anhydrous methanol. The methanol solution at the end of the process contained the hydrophobic neutral fraction (figure 9). To extract the hydrophilic portion of DOM, the effluent was pumped through the AG-MP-50 resin column from which the retained, hydrophilic base was eluted with 1N NaOH (figure 10). This was a deviation from Leenheer's (1981) procedure using 1N NH_4OH to address the concern of possible formation of chloramine in subsequent THM FP study (Korshin *et al.*, 1997). The effluent was then pumped through a third column containing Duolite A7

resin. The effluent was collected as the hydrophilic neutral fraction and the retained was eluted by 2N NaOH as hydrophilic acid fraction and inorganic salts (figure 11). The 2N NaOH was used in place of 3N NH_4OH used by Leenheer (1981) for the same justification described above.

All elutions in this procedure were done in a forward direction or gravity flow (not backflush). This was done to facilitate the recovery procedure. Forward elution was conducted by Day *et al.* (1991) and is the preferred flow configuration for the column.

As a result of the above fractionation technique, 6 fractions of the DOM were isolated based on chemical characteristics. They are termed operationally as hydrophobic base (HPOB), hydrophobic acid (HPOA), hydrophobic neutral (HPON), hydrophilic base (HPIB), hydrophilic acid (HPIA) and hydrophilic neutral (HPIN). All fractions were preserved in the applicable eluting hydrochloric acid or sodium hydroxide and refrigerated at 4°C.

The duolite A-7 has been known to have high resin bleed characteristic, which may interfere with the isolated fraction, specifically the hydrophilic acid fraction. Desalting may be carried out chromatographically as outlined in the original procedure to segregate the inorganic salts from the hydrophilic organic acids. This is accomplished, however, at the expense of potential loss of fractionated material due to volatilization. This was considered highly undesirable for this research. To circumvent this problem, three actions were specifically taken to minimize any possible interference: (1) to wash the resin thoroughly with Milli-Q water until the specific conductance of the effluent is very close to that of the Milli-Q water, (2) to use recycled duolite A-7 (as opposed to

using the virgin resin for the first time) in running actual samples, and (3) to subtract the blank spectrum from an actual spectrum (non-desalting) to ensure quality of data.

The study of DOM using fractionation approach such as the one that is being used in this work is not without valid criticisms. Aiken and Leenheer (1993) and Crum, Murphy and Keller (1996) expressed concerns that since DOM materials must be exposed to extreme pH conditions during the process (i.e., less than 2 and greater than 10) that potential alteration in DOM structure and in natural chlorinated reactivities of the materials may be the consequences. General consensus is fractionation approach via resin adsorption is very tedious and time-consuming. Despite the drawbacks, Thurman (1985) acknowledged that the approach has advanced our fundamental understanding of the nature and behavior of natural organic material in water. Although sample fractionation provided the opportunities to study the mechanism about which DOM interacts with chlorine, it is important to note that the collective behavior of the individual fractions may not be the same as the behavior of the unadulterated water sample in an actual water treatment plant.

4.3 Dissolved Organic Carbon Analysis

DOC was analyzed by an O.I. Analytical 700 system (O.I. Corp., College Station, TX) total organic carbon analyzer using the method of sodium persulfate oxidation (*Standard Methods* 5310-D, 1995). Original source samples were filtered through a 0.45- μ m cellulose filter prior to analysis and fractionation to remove suspended particles. Five percent (5%) phosphoric acid was used to first acidify the sample, which was then purged of total inorganic carbon (TIC) by nitrogen. Sodium persulfate was subsequently

introduced as an oxidant in the process for the oxidation of the organic compounds at 100°C. As CO₂ is purged and trapped at the end of the oxidation process, an infrared photometric beam was used for the analysis of carbon mass. The analyzer was regularly calibrated with 1000-ppm potassium hydrogen phthalate (KHP) standard in either the TIC or total organic carbon (TOC) calibration mode, as recommended by the manufacturer. Each sample was prepared and diluted differently depending on whether the solvent was 0.1N HCl, 1N NaOH or 2N NaOH. The analyzer was programmed accordingly with the proper amount of acid, oxidant and reaction time as recommended by the manufacturer. At least 3 blanks were analyzed prior to the analysis of each sample to establish and verify the appropriate background for quality assurance and control. Duplicates were run randomly.

4.4 DBP Formation Potential (FP) Test

A 7-day chlorine DBP FP test was carried out in accordance with *Standard Methods* 5710B at a chlorine dosage of 100mg/l. Chlorine solution was prepared from calcium hypochlorite in powder form of 69.7% available chlorine. The chlorine dosage of 100mg/l was selected to ensure maximum oxidation of the organic carbon in the sample. This condition of satisfying the maximum demand of the materials involved in the FP test was verified at the end by measuring the residual chlorine in each sample. When no or low residual chlorine was detected (< 2ppm), the test must be repeated. Post FP test data showed a range of residual chlorine of 4 to 6 ppm was attained. All samples were adjusted to a pH of 7 ± 0.2 using 1N HCl and 1N NaOH. The neutralized solution was then buffered with a phosphate solution prior to being incubated at $25 \pm 2^{\circ}\text{C}$ in amber

bottles for 7 days. All bottles were capped head-space free. All sample solutions were prepared using Milli-Q water system. At the end of 7-day chlorine contact time, samples were dechlorinated using ammonium chloride (NH_4Cl) as the sole dechlorinating agent. This was a deviation from the above *Standard Methods* 5710B to be in compliance with the applicable EPA methods 551.1 and 552.2.

4.5 DBP Formation Potential Analyses by Gas Chromatography

The analyses of DBPs which include THMs and HAAs were conducted using a Varian 3400 Gas Chromatograph (Palo Alto, CA) that was equipped with two fused silica capillary columns (0.25mm x 30m), a linearized electron capture detector (ECD), and a Leap Technologies (Carrboro, NC) CTC A200S autosampler. THMs were analyzed in accordance with EPA method 551.1 whereas HAAs by EPA method 552.2. The THMs that were analyzed were chloroform (0.055 ug/L as being the minimum detection level (MDL)), bromodichloromethane (0.003ug/L MDL), dibromochloromethane (0.001 ug/L MDL) and bromoform (0.004 ug/L MDL). HAA_s was analyzed, consisting of 6 analytes— monochloroacetic acid (0.273ug/l MDL), dichloroacetic acid (0.242 ug/L MDL), trichloroacetic acid (0.079 ug/L MDL), monobromoacetic acid (0.264 ug/L MDL), dibromoacetic acid (0.066 ug/L MDL), and tribromoacetic acid (0.820 ug/L MDL). Methyl-tert-butyl-ether was used as the only extraction solvent in this method. Bromofluorobenzene (Ultra Scientific) and decafluorobiphenyl (Ultra Scientific) were used as internal and surrogate standard, respectively for THM-HAN analysis. For HAAs analysis, the internal standard used was 1,2,3-trichloropropane (Supelco) and the surrogate standard was 2,3-dibromopropionic acid (Supelco). All extracts were analyzed

within 24 hours of the completion of the liquid-liquid-extraction (LLE) procedure. After the analyses, the sample bottles were secured with new caps and stored in freezer at -10°C . Data were collected and processed by the MiniChrome v. 1.60 software package (VG Data Systems, Cheshire, U.K.)

4.6 SFS Analyses by Fluorescence Spectrophotometer

Fluorescence measurement was accomplished by the use of the Hitachi F-3010 spectrophotometer (Tokyo, Japan).

Raw data was recorded by a computer in the form of PRN files for each excitation wavelength ranging from 225nm to 525nm. Each excitation was then scanned and the emission recorded for the range up to 633nm. The program was set for an optimal stepwise increment of 12nm both with respect to the excitation as well as the emission. Raw data was then fed into a Grams5 software (Galactic Inc, Mass.), which converted each PRN file into a SPC file. Each spectral SPC file was linked together via a multifile utility from which a full 3-D spectral can be viewed at any desired angle. The multifile spectral can be integrated for the total area under the curve (via WORD and Excel spreadsheet). Spectral subtraction can also be done to screen out the known undesirable components of the total spectral. These were among the math functions that were employed in this research. The program was also designed to scan the test specimen in either one of the 2 modes__ forward mode from low excitation wavelength (high energy state) to high excitation wavelength (low energy state) or reverse mode. This research was done on reverse-mode scanning as a precaution to not causing any damage to the

sample molecules. Our data showed that, for the equipment being used, either mode of scanning operation was equally acceptable.

A model of Spectral Fluorescent Signature (SFS) database was created by fractionating the sourcewater sample into 6 different fractions as mentioned earlier (figure 3). Seven concentrations were established from each fraction ranging from 0.1ppm to 2ppm. Each concentration was then subjected to a fluorescent spectrophotometric analysis in accordance with the analytical protocol.

CHAPTER 5

METHOD DEVELOPMENT FOR DOM PRECURSOR IDENTIFICATION AND DBP FORMATION POTENTIAL COMPUTATION

5.1 Identification of DOM Fractions Using Spectral Fluorescent Signature (SFS)

To establish a background for the rationality in using SFS as a tool leading to the identification of DOM fractions, it is necessary to briefly discuss the fluorescence phenomenon. When a substance absorbs radiant energy such as ultraviolet rays, alpha, beta gamma rays, X-rays, cathode rays and visual lights, the atom is raised to a higher level (White *et al*, 1970). In this excitation process, a discrete quantum of light energy is absorbed. The amount of energy is equal to the difference in the two energy levels, which is characteristic of each substance being scanned. When the excitation ceases, the substance returns to the original atomically stable state. In doing so, it emits the energy that was previously absorbed. The emission of light in this case is called fluorescence if it lasts about 10^{-8} seconds or shorter; otherwise it is called phosphorence (White *et al*, 1970). It was found from this study that the slope, or the angle, by which the energy is emitted during the process of fluorescence, is more characteristic of a particular NOM fraction than the intensity as shown in the SFS-catalog of figures in appendix A (A4-A16).

From the physics of fluorescence, the characteristic angle of a particular fraction can be viewed as the primary signatory component of that fraction. This characteristic results from the fact that as a particular fraction fluoresces, it does so in a quantized fashion. As a consequence, there is no middle ground or in-between energy level

emission. This is important because it provides a key building block to the characteristic of spectral fluorescent signatures of the fractions under study.

SFS in this research is defined as the process of subjecting each reasonably finite component (fraction) of DOM to fluorescence scanning in accordance with section 4.6. The resultant unique spectral fluorescent characteristic of signature (hence the term SFS) is examined and analyzed. Specific spectral feature such as location of the fluorescent peak, intensity, concentration, spectral area, slope of the peak and shape factor are digitized in a database. When the sample of the whole water sample is scanned, the full spectrum is searched using the digitized SFS to identify the precursors that make up the sample in question.

Using the research protocol of figure 3, a total number of 144 signatures of the fractions of different concentrations have been generated whose patterns have been examined. Each fraction can be characterized by its peak slope (S_p), its spectral area (A_p) and more specifically, its shape factor (SF). The shape factor is defined in the following way:

$$SF = (S_p) * (A_p)$$

Each of the six isolated fractions of the intake water was subjected to a fluorescent spectrophotometric scan (i.e. SFS). The resultant spectral fluorescence properties are shown in table 8. Four of the six fractions' SFSs revealed two peaks; peak that is associated with higher level of excitation energy (i.e. lower excitation wavelength) is termed "major peak" and that associated with the lower excitation energy is termed "minor peak". Only major peaks were found to play important role in this method development section.

Table 8 Locations of the Six DOM Fractions Peaks

Fraction	Major Peak Location	Fluorescence Angle (degree)
Hydrophobic Base	(225-237 Ex.; 340-368 Em)	68
Hydrophobic Acid	(237-249 Ex.; 367-404 Em)	55
Hydrophobic Neutral	(225-237 Ex.; 321-327 Em)	84
Hydrophilic Base	(225-237 Ex.; 355-379 Em)	55
Hydrophilic Acid	(225-237 Ex.; 359-388 Em)	56
Hydrophilic Neutral	(225 Ex.; 592-600 Em)	50

The locations and spectral slopes of the fractions as described in table 8 above were statistically determined from a compilation of 144 signatures at 95% confidence level. As shown in the table, the peaks of the fractions are quite distinctive in fluorescing locations as indicated by the excitation and emission wavelength ranges. The major spectral peaks all have essentially the same excitation wavelengths (225-237 nm), except for hydrophobic acid (237-249 nm), which is the high-energy end of the wavelength spectrum examined. Spectrally, what set these fractions apart are the emission wavelengths. The exception is noted in the neutral fraction categories where hydrophobic fraction was distinctively shown to fluoresce at higher wavelengths than the hydrophilic fraction. These observations give rise to grouping the DOM fractions in accordance with energy emission. Figure 12 is a contour SFS of a typical raw water sample showing the major peak regions of the six fractions when examined separately.

An examination of the SFSs of the fractions (ref. figure A4-A16) revealed other distinct characteristics. The rising slope of the spectral peak, S_{rp} , (slope between the lowest Em (i.e. Ex + 24 nm) and the major fraction spectral peak) and the emission spectrum area in which the major peak exists (A_p) for each fraction are also characteristics of the fractions. The six fractions were identified qualitatively by

examining their corresponding SFSs. For example, the two neutral fractions SFSs were readily identified because of the single-peak feature that occurs at the high end of the excitation energy spectrum (225-237 nm range). Although they are similar in this region, an examination of the emission spectra showed that rising slopes pertaining to the peaks of hydrophobic neutral fractions are larger than those of the hydrophilic neutral fractions. In addition, the integration of the peak emission spectral is also larger for the hydrophobic neutral fraction compared to the hydrophilic neutral. And so, despite the fact that the two fractions' major peaks are overlapped in the same fluorescing region, hydrophobic neutral and hydrophilic neutral fractions can be distinguished based on factors such as S_{rp} and A_p of spectra as shown later.

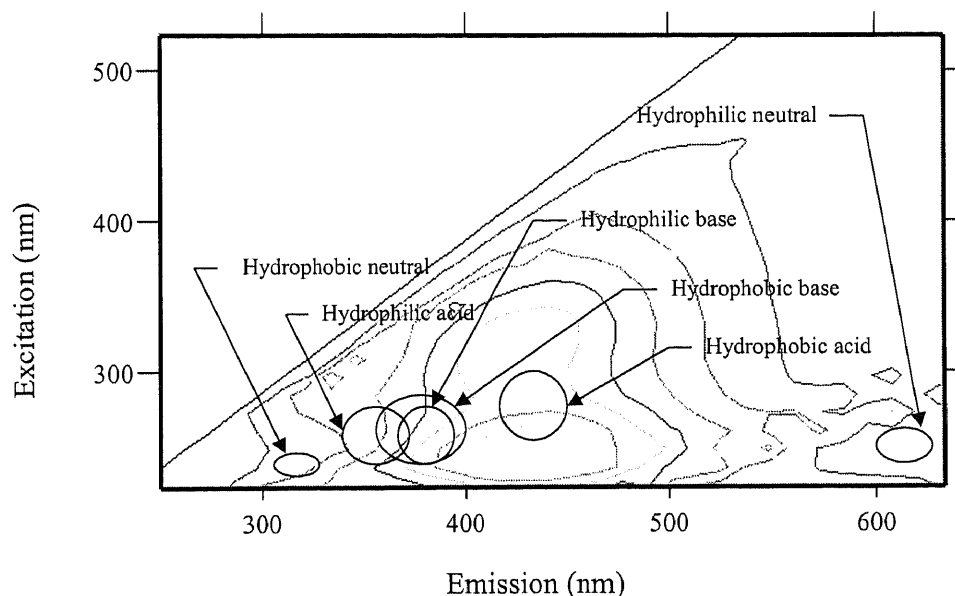


Figure 12 Contour of a Raw Water SFS (Raritan-Millstone River in Bound Brook, NJ, May 21, 1998) and Major Regions Where Fractions' Peaks Were Found to be Unique When Examined Separately (see table 8).

Being a signature, each is expected to be unique in some aspects despite the fact that they may appear to be overlapped with each other in some cases. The following section will discuss how the database of SFS signatures can be used to determine the concentration of the precursors.

5.1.1 Determination of Fraction's Concentration by SFS

To relate spectral features of raw water SFS to fraction concentrations, it was found, through trial and error, that there are 3 tiers of identification criteria that can be used in certain combination for identification. They are (a) the emission spectrum passing through the major peak of the corresponding fraction, (b) the rising slope of the spectrum, S_{rp} and (c) the integration, or area, of the spectrum, A_p . It's important to note here that the above 3 tiers do not involve the spectral intensity, as it was not apparent to be a characteristic of the corresponding fraction concentration. Table 9 includes the SFS database that was developed from individual fraction SFSs and used to determine the fraction qualitatively and quantitatively from a raw water SFS, as described later.

The database as shown in table 9 was constructed starting with each fraction of the intake water sample being diluted into different concentrations (0.1, 0.2, 0.4, 0.6, 0.8, 1.0 ppm). Each concentration was subject to a full fluorescent scan as described in section 4 previously. Each scan produced 26 emission spectra which were then linked together to yield a complete spectral fluorescent signature (SFS) featuring 3 axes which include excitation, emission and intensity. Figure 13 shows a typical SFS of hydrophilic acid fraction:

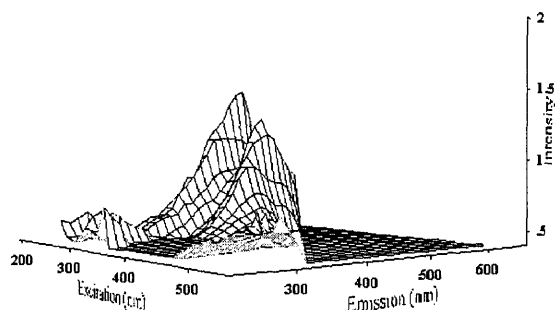


Figure 13 Spectral Fluorescent Signature (SFS) of a Typical Hydrophilic Acid Fraction at 0.4 ppm (May 21, 1998 – intake R/M WTP)

From the SFS, the emission spectra that pass through the major peak locations of the six fractions are selected (figure 12). Through trial and error, it was found that the product of the rising slope of the spectrum, S_{rp} , and the integral value, or area, of the spectrum, A_p , were function of the corresponding fraction concentrations. The concept of spectrum's shape factor, SF, is introduced as the product of the spectral area A_p and the rising slope of the peak spectrum, S_{rp} (figure 14).

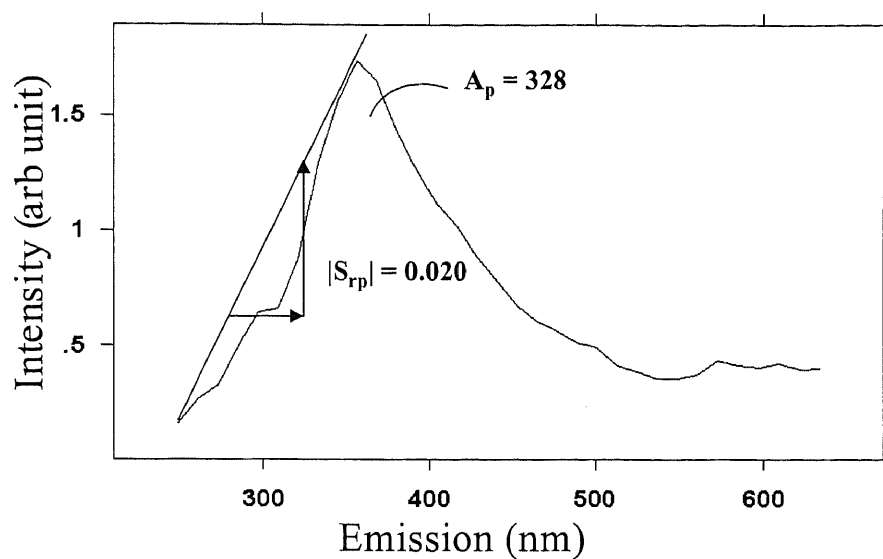


Figure 14 A Peak Spectrum of Hydrophilic Acid Fraction at 0.4 ppm.
Excitation Wavelength Was at 225 nm. SF is 4.3

Table 9: SFS Database of Individual Fractions

Fraction	Conc.	A_p	S_{rp}	$S_{rp} * A_p$	Fraction	Conc.	A_p	S_{rp}	$S_{rp} * A_p$
HPOB	0.1	330	0.009	2.85	HPIB	0.1	486	0.006	2.92
	0.2	378	0.018	6.89		0.2	402	0.006	2.41
	0.4	620	0.038	23.70		0.4	373	0.0086	3.21
	0.6	572	0.039	22.40		0.6	327	0.0124	4.05
	0.8	474	0.022	10.32		0.8	336	0.0143	4.80
	1.0	478	0.032	15.56		1.0	361	0.0130	4.69
	2.0	396	0.010	3.77		2.0	394	0.0274	10.80
HPOA	0.1	290	0.0025	0.72	HPIA	0.1	349	0.0134	4.68
	0.2	383	0.0053	2.04		0.2	328	0.0152	4.99
	0.4	511	0.0098	5.01		0.4	339	0.0196	6.64
	0.6	629	0.0156	9.83		0.6	638	0.0692	44.15
	0.8	719	0.0214	15.40		0.8	313	0.0175	5.48
	1.0	825	0.0258	21.30		1.0	271	0.012	3.18
	2.0	1105	0.0490	54.60		2.0	456	0.0108	4.92
HPON	0.1	446	0.0295	13.20	HPIN	0.1	261	0.0023	0.60
	0.2	530	0.047	24.90		0.2	271	0.0028	0.76
	0.4	667	0.0897	59.80		0.4	411	0.0046	1.90
	0.6	840	0.109	91.20		0.6	267	0.0027	0.72
	0.8	997	0.196	195.00		0.8	432	0.0095	4.10
	1.0	1187	0.2790	331.00		1.0	462	0.0094	4.34
	2.0	2135	0.2160	460.00		2.0	329	0.0029	0.95

In addition to the above database, there are correlations prepared as shown in table 10 below in case a good match cannot be located.

Table 10 SFS-Concentration Correlations. SF being the Shape Factor of the Spectrum under Consideration—a Product of Spectral Area and Spectral Slope

Fraction	Correlation	R Coefficient
Hydrophobic Base Fraction	Concentration = $0.26 (SF) + 0.02$	0.95 (n=7)
Hydrophobic Acid Fraction	Concentration = $0.03 (SF) + 0.20$	0.86 (n=9)
Hydrophobic Neutral Fraction	Concentration = $0.15 (SF) + 0.31$	0.99 (n=6)
Hydrophilic Base Fraction	Concentration = $0.05 (SF) + 0.11$	0.91 (n=7)
Hydrophilic Acid Fraction	Concentration = $0.20 (SF) + 1.08$	0.97 (n=7)
Hydrophilic Neutral Fraction	Concentration = $17.31 (SF) + 0.01$	0.98 (n=7)

The following is a discussion and demonstration of the potential use of this SFS technique in the area of water treatment to rapidly determine the concentration of each DOM fraction in a particular water sample.

1. Sample the water and subject it to a 0.45-um filtration to obtain DOM.
2. Scan the filtered sample with a fluorescent spectrophotometric instrument at Ex 225, 237, and 249 nm (per table 8 Ex windows) over Em = (Ex + 24 nm) to 633 nm, with a 12 nm increment.
3. Select the emission spectrum or spectra that correspond(s) to the location of the major peak of the fraction of concern (see table 8).
4. Compute the tangent to the spectrum at the midpoints of the Em window of the corresponding fraction (S) and the integral of the corresponding spectrum defined by the Em window limits (A) (see figure 15).
5. Determine S*A, which is the shape factor (SF)
6. Input SF into the FractionID, which is a component of a computer code. The FractionID will use the variable SF as the criteria in searching the database of the

corresponding fraction (e.g. table 9, $S_{rp} * A_p$) for the best match. Once the best match is determined, the corresponding fraction concentration is determined.

If the best match cannot be located, the code will then resort to built-in correlation for a particular fraction to calculate the concentration of the fraction (table 10)

7. Select another fraction and return to step 3, until all fractions are determined.

As described above, through trial and error, it was also found that the spectral shape factor $S * A$ as the matching criteria with the $S_{rp} * A_p$ of the individual fractions (see Table 9). Realizing that exact matching is a rare possibility, percentile tolerances must be applied due to the limited data in the database developed in this preliminary work.

The following figure 15 illustrates how the fraction could be identified on the whole (non-fractionated) raw water spectrum by using spectral slope at a point (derivative) and the area under the spectral curve (integration) within the emission limits for that particular fraction.

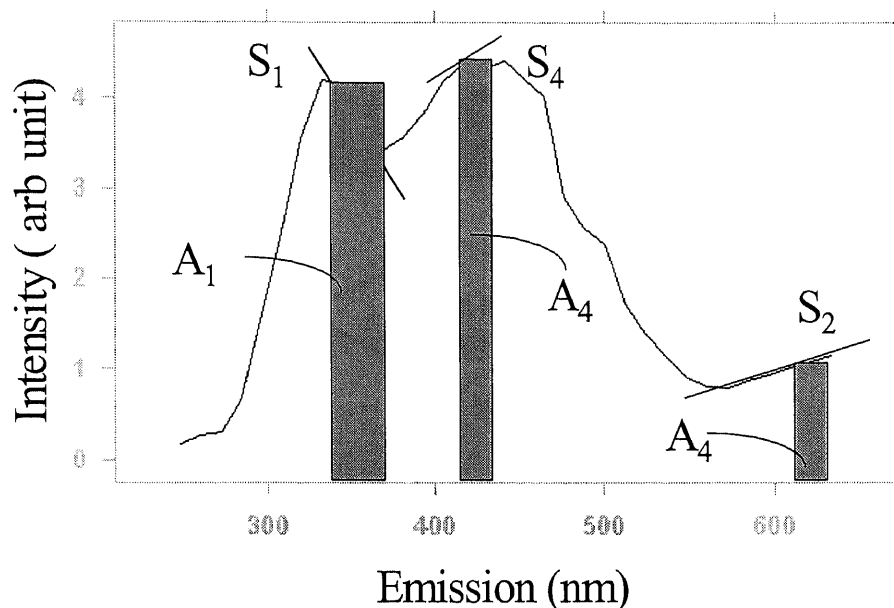
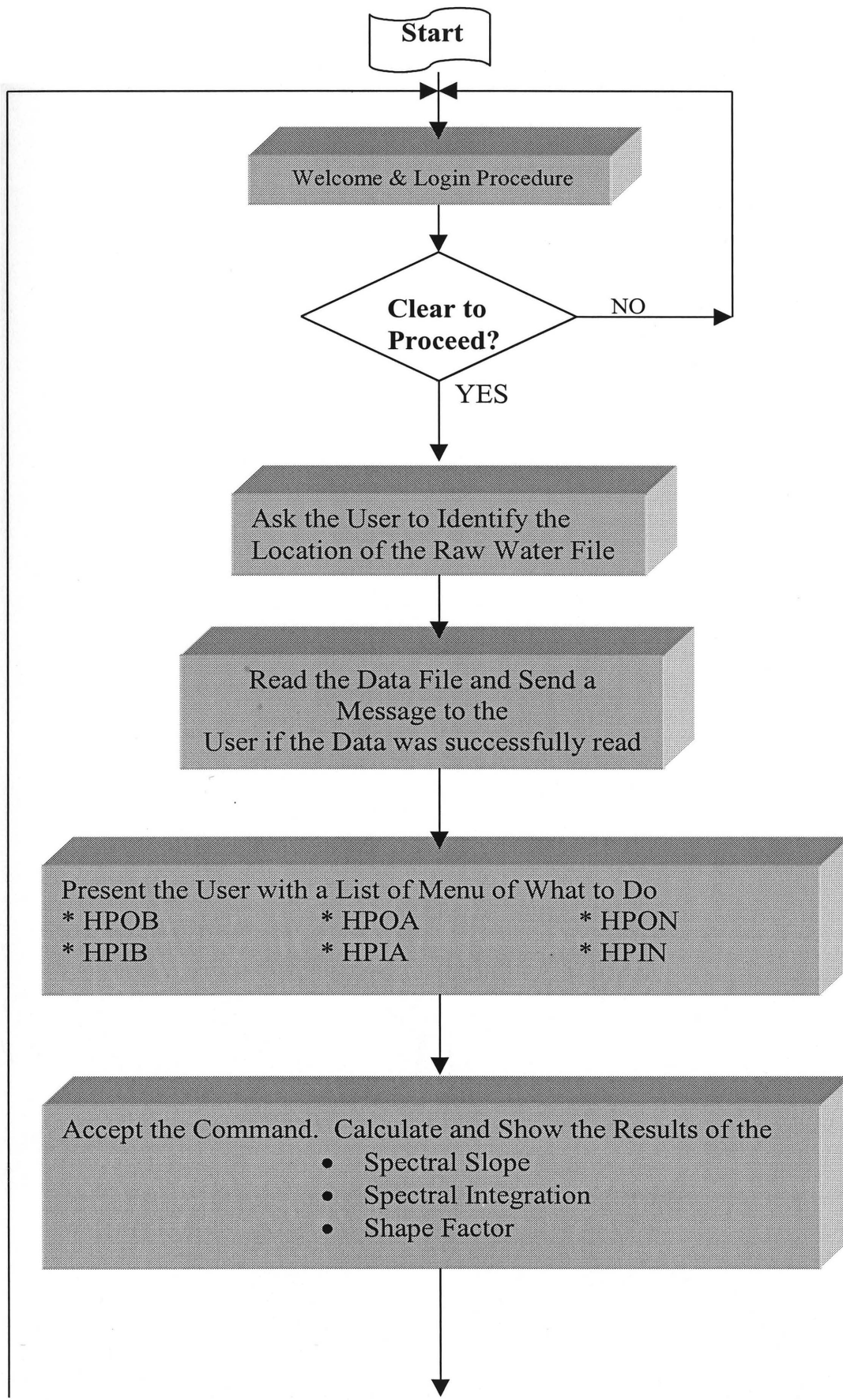


Figure 15 An Illustration of How the Spectral Slopes and Areas Are Computed. S_1 is the tangent to the spectrum at the mid-point of the two Em limits of hydrophilic acid. A_1 is the correspondent integration of the portion of the hydrophilic acid spectrum whose limits are the lower and upper Em values (table 8). Similarly, S_2 and A_2 are those values applicable to hydrophilic neutral fraction; S_4 and A_4 are applicable to hydrophobic acid fraction

5.1.2 Computer Code Development

To manage the vast amount of SFS data so that determination of each fraction's concentration can be expediently made, a computer code was developed based on graphical user interface features. Visual Basic (v. 5) was used as a means of coding. The program is listed in appendix B in its entirety. The following is a flowchart of the program:



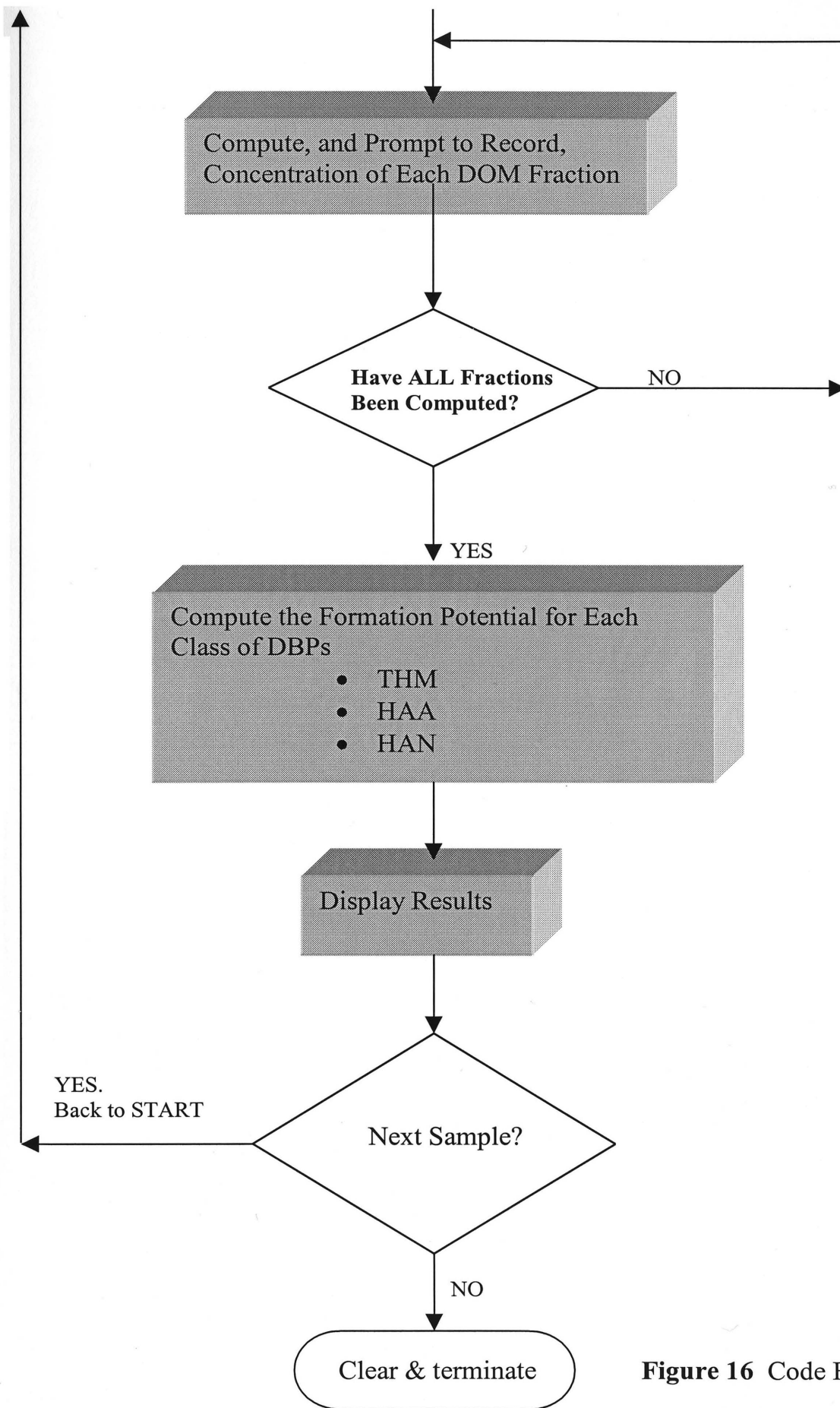


Figure 16 Code Flowchart

5.1.3 Method Validation

To validate the SFS toolkit, water samples at all unit operation locations were taken, fractionated and measured for concentrations. These were recorded as actual or known data. The SFS toolkit was then used on to scan each of the original, non-fractionated sample at the spectrally known location of each fraction. Going through the method, which was designed into the computer code, the SFS toolkit produced a predicted concentration for each fraction. The predicted concentration was compared to the known concentration. Data were analyzed using Statistica software package. Correlations of the pair of variables, which are predicted concentration and actual concentration, were accomplished using Anova analysis of variation.

The following are samples of the validation (table 11 and 12). More analyses of the results are presented in section 6.4.

Table 11. Summary of Validated Results. Samples from EWC WTP. Fraction Concentration in ppm.

Fraction	EWC CR Influent (5/21/98)		EWC CR Effluent (5/21/98)	
	Predicted	Observed	Predicted	Observed
HPOA	0.40	0.50	0.20	0.20
HPOB	0.10	0.20	0.03	0.10
HPON	0.60	0.70	0.30	0.50
HPIA	2.00	1.80	1.10	1.10
HPIB	0.10	0.20	0.10	0.20
HPIN	0.80	0.80	0.10	0.20

Table 12. Summary of Validated Results. Samples from PVWC WTP. Fraction Concentration in ppm.

Fraction	PVWC Influent (4/28/98)		PVWC R/M Effluent (4/28/98)	
	Predicted	Observed	Predicted	Observed
HPOA	0.50	0.50	0.20	0.20
HPOB	0.80	0.30	0.20	0.20
HPON	0.50	0.50	0.30	0.30
HPLA	2.40	2.30	1.30	0.80
HPIB	0.30	0.30	0.20	0.20
HPIN	0.50	0.60	1.00	0.20

Figure 17 and 18 were used to predict the concentration of the HPOA fraction as shown below:

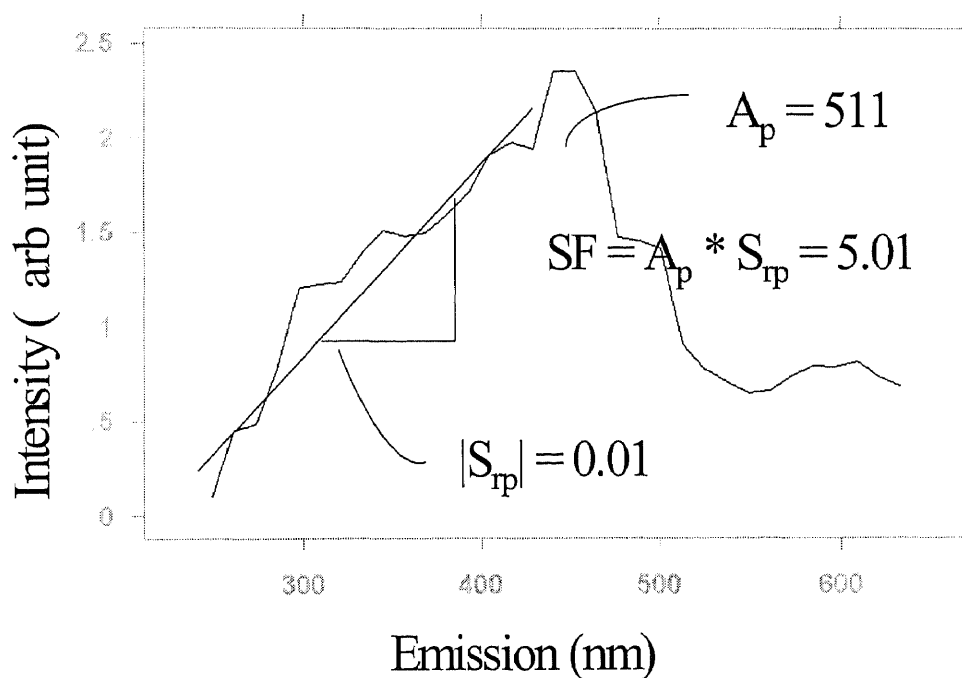


Figure 17 Spectrum of the Hydrophobic Acid Fraction at 0.4 ppm Showing the Shape Factor SF and its Components. See Figure 18 for Matching.

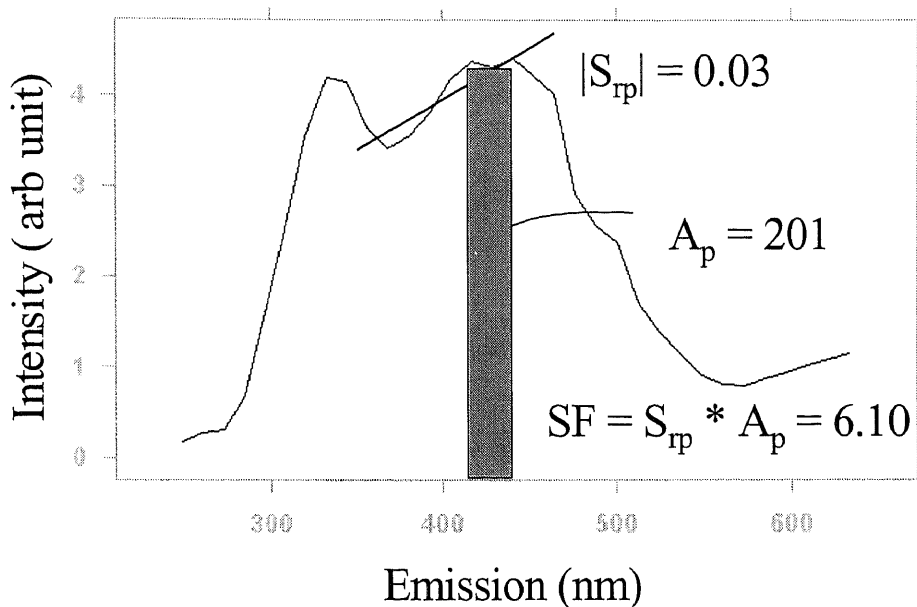


Figure 18 The Hydrophobic Acid Fraction at 0.4 ppm Shown on a Raw Water Intake Water Spectrum. SF factors are being matched.

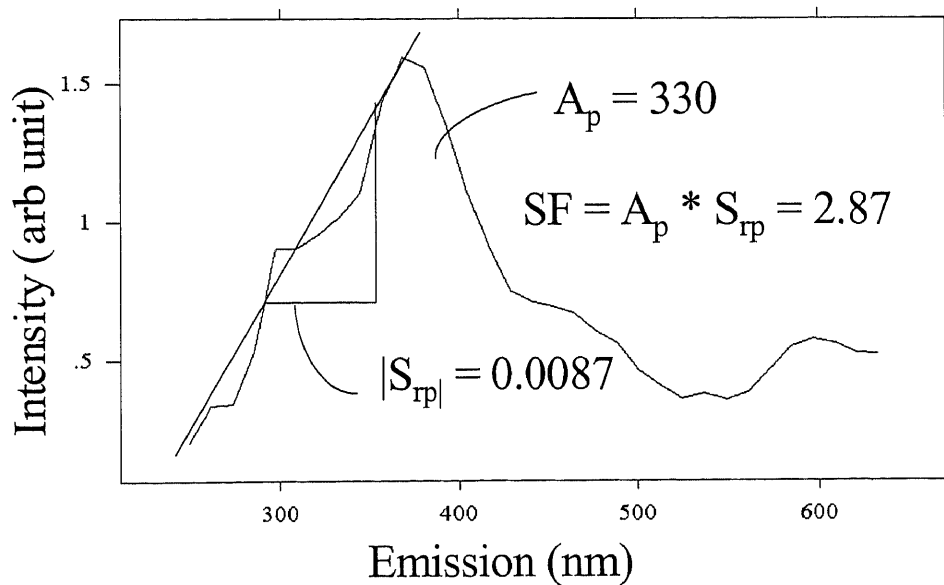


Figure 19 Spectrum of the Hydrophobic Base Fraction at 0.1 ppm showing the Shape Factor SF and its Components. See Figure 20 for Matching.

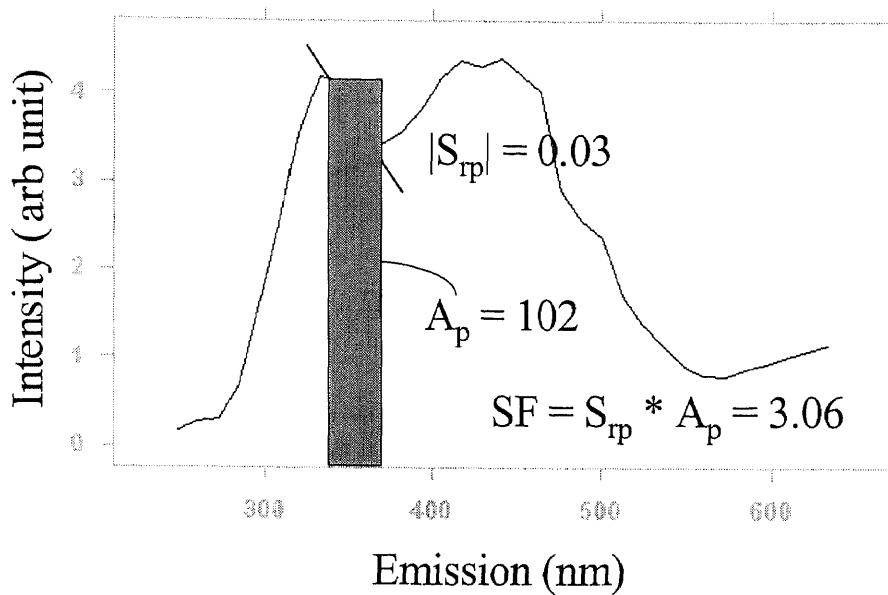


Figure 20 The Hydrophobic Base Fraction at 0.1 ppm Shown on a Raw Water Intake Water Spectrum. SF factors Are Being Matched.

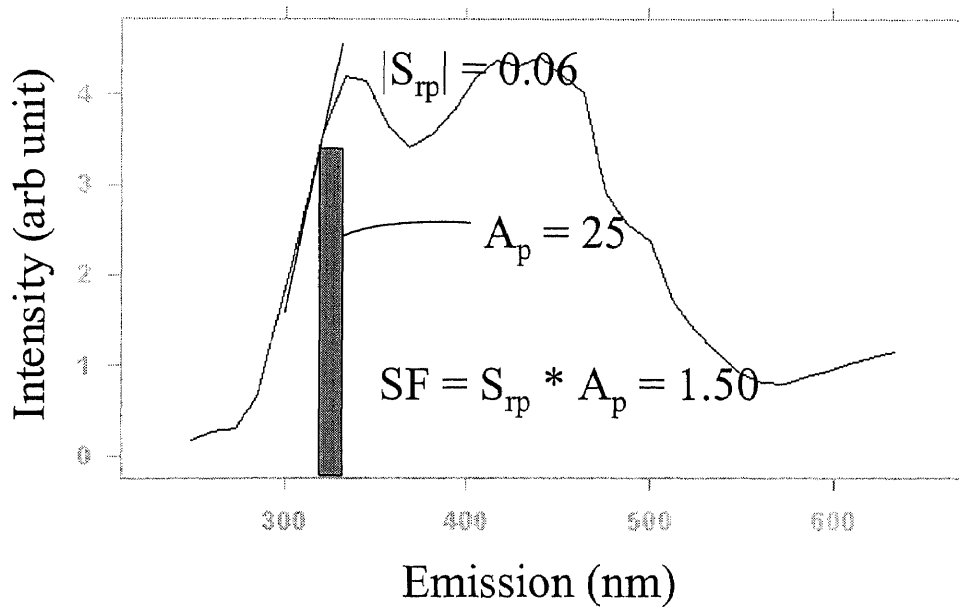


Figure 21 The Hydrophobic Neutral Fraction at 0.7 ppm Shown on a Raw Water Intake Water Spectrum. SF Factor Cannot Be Matched. Correlation is being used (figure 22).

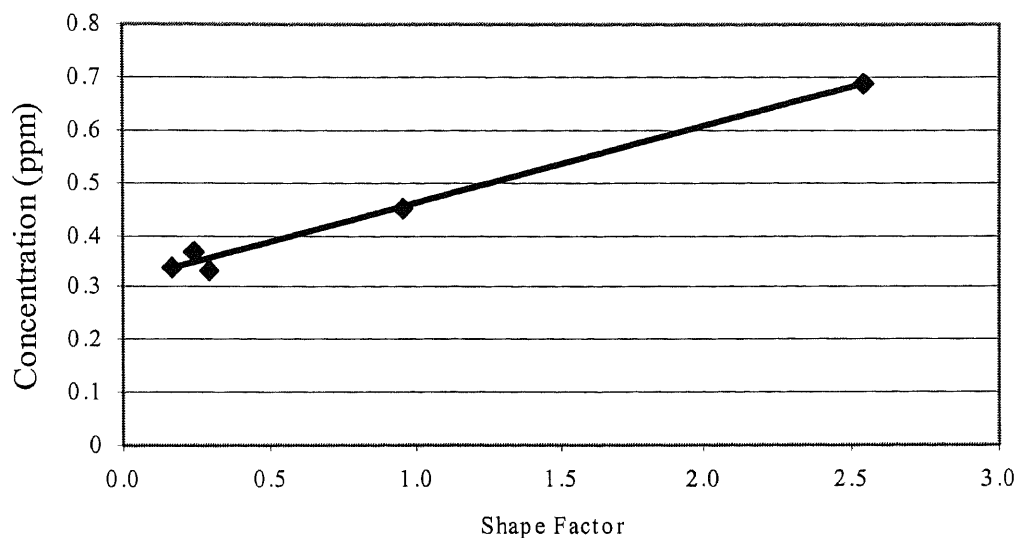


Figure 22 Fraction Concentration-Shape Factor Correlation is Being Used for the Calculation since there is no match in the SFS Database. $y = 0.15x + 0.31$; $R = 0.99$; $n = 5$

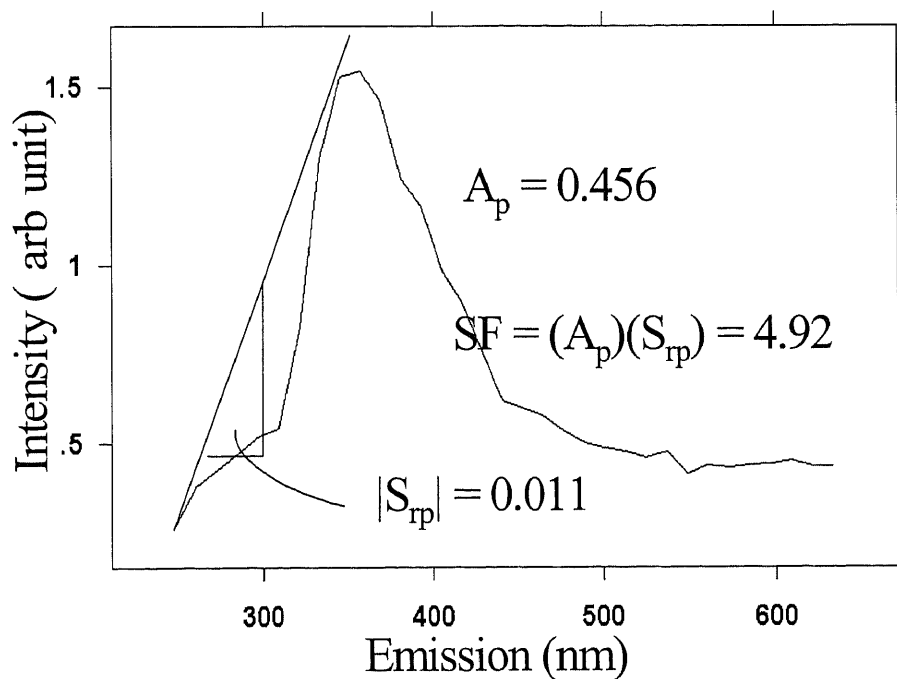


Figure 23 Spectrum of the Hydrophilic Acid Fraction at 2 ppm Showing the Shape Factor SF and its Components. See Figure 24 for Matching.

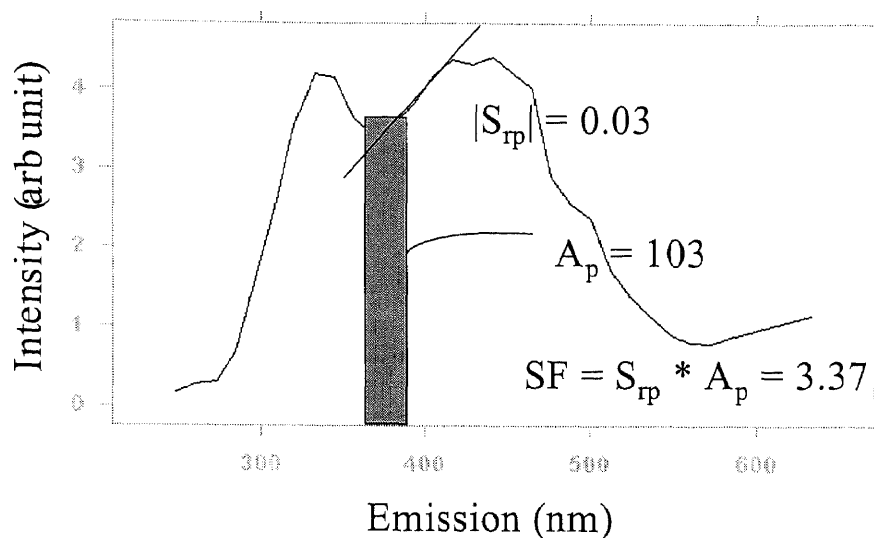


Figure 24 The Hydrophilic Acid Fraction at 2 ppm Shown on a Raw Water Intake Water Spectrum. SF factors are being matched.

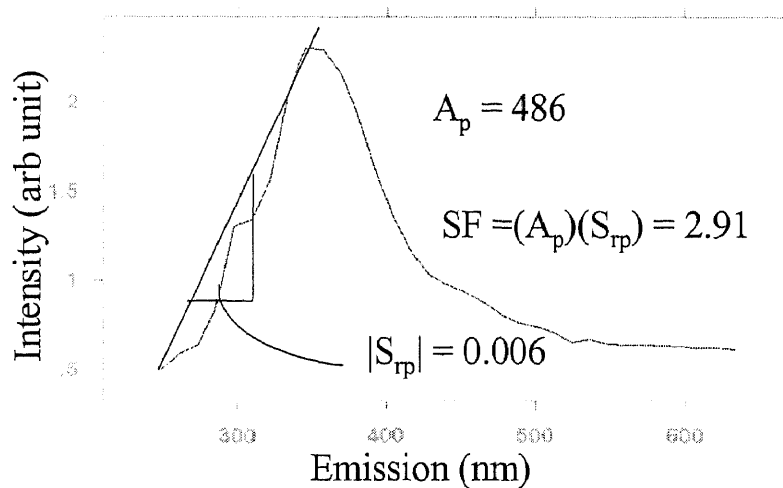


Figure 25 Spectrum of the Hydrophilic Base Fraction at 0.1 ppm Showing the Shape Factor SF and its Components. See Figure 26 for Matching.

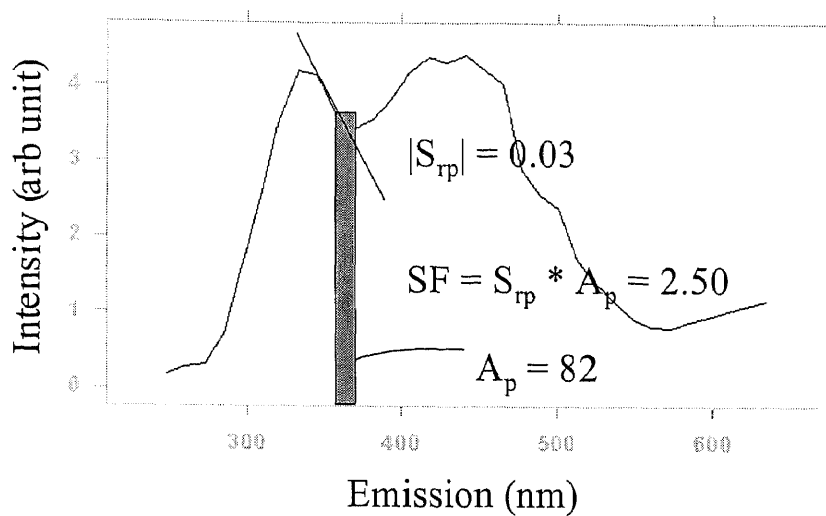


Figure 26 The Hydrophilic Base Fraction at 0.1 ppm Shown on a Raw Water Intake Water Spectrum. SF factors are being matched.

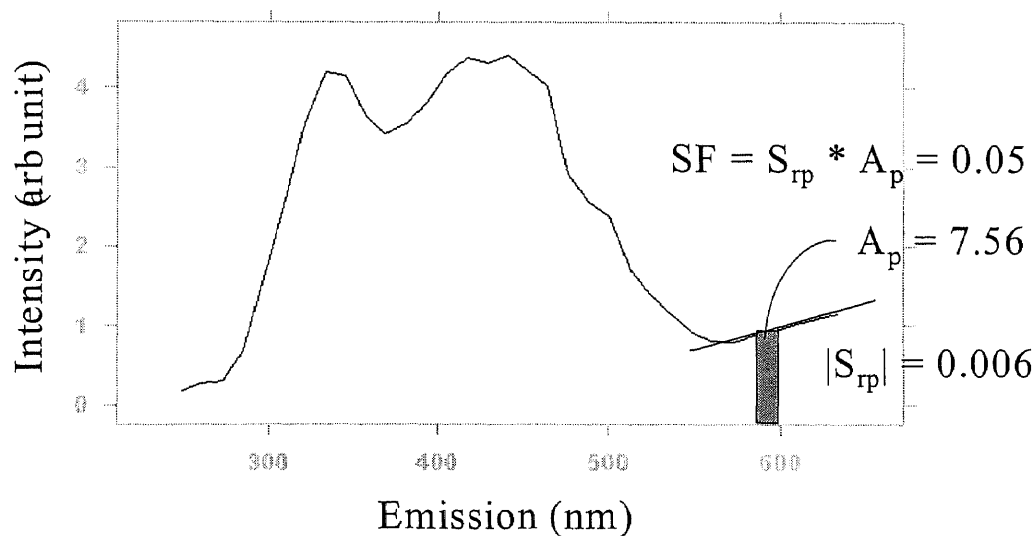


Figure 27 The Hydrophilic Neutral Fraction at 0.8 ppm Shown on a Raw Water Intake Water Spectrum. SF factor cannot be matched. Correlation is being used (figure 28).

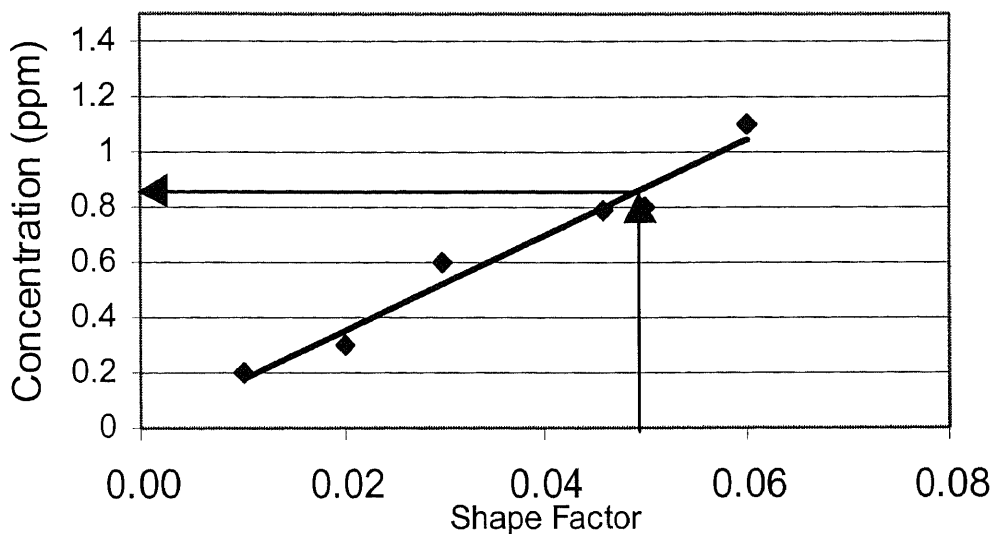


Figure 28 Fraction Concentration-Shape factor Correlation Is Being Used for the calculation since there is no match in the SFS Database. $y = 17.31(x) + \text{Used } 0.01$; $R = 0.98$; $n = 6$

5.2 Determination of DBP FP of Raw Water by SFS-GC Database Cross-Linking

As in the case of the SFS database, the database for the formation potential of precursors was also built by conducting the formation potential test for each fraction as outlined in the research protocol (figure 3) and by the methods as discussed in section 4.3 and 4.4.

The following is the DBP FP database:

Table 13 DBP Formation potential of DOM fractions

Fraction	Concentration (mg/l)	Formation Potential (ug/mg DOC)	
		THMs	HAAs
HPOB	0.1	4.8	0.2
	0.2	7.1	0.3
	0.4	9.3	0.4
	0.6	10.5	0.4
	0.8	16.6	0.6
	1	12.2	0.9
	2	11.1	1.0
HPOA	0.1	7.2	0.2
	0.2	8.6	1
	0.4	7.9	0.5
	0.6	8.6	1.0
	0.8	20.7	0.3
	1	16.1	0.9
	2	14.7	8.3
HPON	0.1	11.7	-
	0.2	16.3	0.6
	0.4	24.4	21
	0.6	18.0	30
	0.8	21.6	23
	1.0	18.9	43
	2.0	45.5	21
HPIB	0.1	7.2	0.5
	0.2	9.2	0.5
	0.4	10.8	0.8
	0.6	11.2	0.5
	0.8	9.8	0.6
	1.0	8.0	0.2
	2.0	15.0	1.7
HPIA	0.1	11.6	0.8
	0.2	20.2	0.6
	0.4	38.9	2.7
	0.6	32.2	1.7
	0.8	33.3	2
	1.0	33.2	5.5
	2.0	19	7.5
HPIN	0.1	9.5	1.2
	0.2	18.2	1.8
	0.4	28.1	1.7
	0.6	27.4	2.8
	0.8	34.1	3.5
	1.0	-	
	2.0	-	

5.2.1 The DBP FP Correlations

The correlation of NOM Fractions at Standard Conditions (pH of 7 and 25 deg. C).

In an effort to establish a database that can relate the raw water DOC with the formation potential of each of its NOM fraction, each sourcewater intake sample was fractionated into 6 different fractions. Each fraction was then used to prepare sample solutions at 7 different concentrations from 0.1ppm to 2 ppm. Experiments were conducted in accordance with the following protocol:

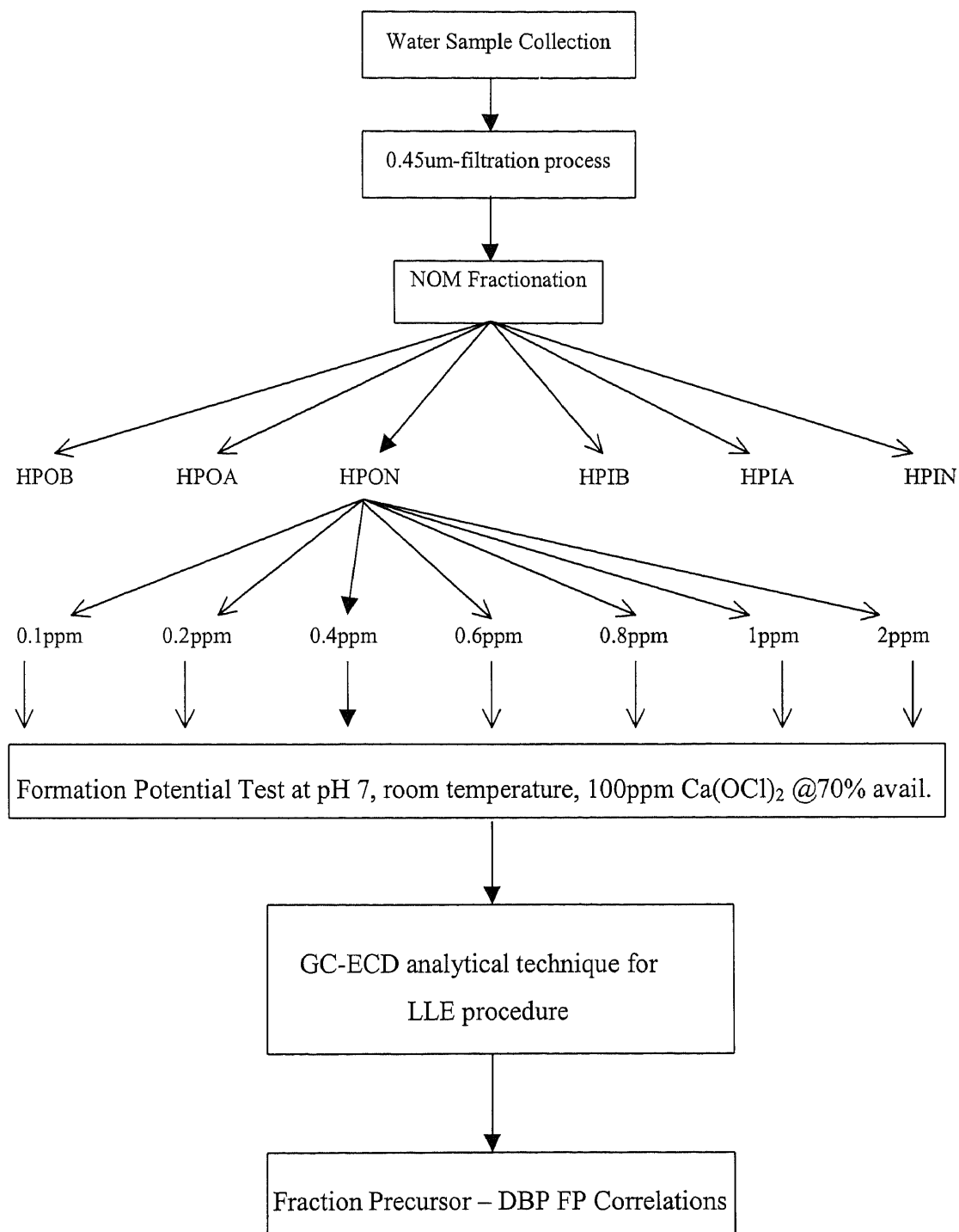


Figure 29 Protocol for DBP FP test and liquid-liquid extraction procedure

Under the above standard conditions of the formation potential test, the following are the empirical relationships between DBPs and the NOM fraction concentration.

5.2.1.1 Trihalomethanes:

Hydrophobic Base (HPOB) Fraction

$$\text{THM FP (ug/mg DOC)} = 7.53 (\text{HPOB ppm}) + 5.36 \quad R = 0.95$$

n = 5

Hydrophobic Acid (HPOA) Fraction

$$\text{THM FP (ug/mg DOC)} = 3.85 (\text{HPOA ppm}) + 6.83 \quad R = 0.98$$

n = 5

Hydrophobic Neutral (HPON) Fraction

$$\text{THM FP (ug/mg DOC)} = 17.22 (\text{HPON ppm}) + 9.88 \quad R = 0.97$$

n = 5

Hydrophilic Base (HPIB) Fraction

$$\text{THM FP (ug/mg DOC)} = 3.49 (\text{HPIB ppm}) + 8.37 \quad R = 0.94$$

n = 5

Hydrophilic Acid (HPIA) Fraction

$$\text{THM FP (ug/mg DOC)} = 23.46 (\text{HPIA ppm}) + 13.43 \quad R = 0.92$$

n = 5

Hydrophilic Neutral (HPIN) Fraction

$$\text{THM FP (ug/mg DOC)} = 31.41 (\text{HPIN ppm}) + 10.10 \quad R = 0.94$$

n = 5

5.2.1.2 Haloacetic Acids:

Hydrophobic Base Fraction

$$\text{HAA FP (ug/mg DOC)} = 0.49 (\text{HPOB ppm}) + 0.17 \quad R = 0.95$$

$$n = 5$$

Hydrophobic Acid Fraction

$$\text{HAA FP (ug/ml DOC)} = 4.34 (\text{HPOA ppm}) - 0.68 \quad R = 0.98$$

$$n = 5$$

Hydrophobic Neutral Fraction

$$\text{HAA FP (ug/mg DOC)} = 48.40 (\text{HPON ppm}) - 3.52 \quad R = 0.96$$

$$n = 5$$

Hydrophilic Base Fraction

$$\text{HAA FP (ug/mg DOC)} = 0.66 (\text{HPIB ppm}) + 0.27 \quad R = 0.95$$

$$n = 5$$

Hydrophilic Acid Fraction

$$\text{HAA FP (ug/mg DOC)} = 0.6 (\text{HPIA ppm}) + 2.6 \quad R = 0.93$$

$$n = 5$$

Hydrophilic Neutral Fraction

$$\text{HAA FP (ug/mg DOC)} = 3.11 (\text{HPIN ppm}) + 0.89 \quad R = 0.96$$

$$n = 5$$

It has been shown from this section that the disinfection by-product problem under consideration is a two-part problem. Part one is to determine the concentration of each fraction of DOM that has the potential to react with chlorine. Solutions from part one are then fed into part two of various correlations to determine the formation potential of the sought-after class of DBP. An example problem is given in the proposed application of the method (section 6).

CHAPTER 6

RESULTS AND DISCUSSION

6.1 Fraction Mass Balance

Mass balance confirms the effectiveness of the fractionation procedure giving a 10-15% tolerance of DOM recovery. Day *et al.* (1991) reported similar tolerance, which was due to loss of the hydrophilic acid fraction from the strong anionic nature of the AG-MP-1 resin. Variations from 8-12% were also reported by Croue *et al.* (1993). Surplus recovery in this study was probably due to the contribution of inorganics that were introduced in the process such as HCl and NaOH for acidity adjustment as well as elution. Rotary vacuum evaporation of the fractions were not conducted because concentrated forms of the isolated fractions were not of interest to the study and certainly not at the expense of “considerable” losses of the volatile organic compounds (Schnoor *et al.*, 1979). Although the process is time-consuming, it provided the opportunity to isolate the components of the DOM and ascertain their respective reactivity with oxidants to form DBPs. The fractionation procedure was repeated five times for different ICR sampling points in the treatment plants prior to actually implementing the experimental strategy to statistically confirm the precision of the results, which are shown in table 14 below:

Table 14 Repeatability of Fractionation Procedure

Trial #	DOC (mg)	HPOB (mg)	HPOA (mg)	HPON (mg)	HPIB (mg)	HPIA (mg)	HPIN (mg)	%Diff
1	34.02	2.03	4.13	6.21	1.32	16.44	7.07	9.35
2	41.58	2.95	4.84	4.08	2.23	21.12	5.40	-2.34
3	31.59	2.60	3.06	4.56	2.21	12.40	3.60	-10.02
4	18.00	1.77	2.90	3.32	2.49	8.25	1.85	14.27
5	16.79	1.88	2.16	3.02	2.05	7.27	1.80	8.23
Stdev.		0.51	1.06	1.26	0.44	5.78	2.29	

It was noted in table 15 below that the findings were in agreement with those reported by others (Amy, 1993; Bose, 1994) in that ozonation does not change the DOC concentrations substantially.

Table 15 Mass Balance of DOM Fractions along the Treatment Trains

		MASS (mg)								
Plant Location		DOC	Sum Fractions	HPOB	HPOA	HPON	HPIB	HPIA	HPIN	% surplus
CR	Intake	34.02	37.2	2.03	4.13	6.21	1.32	16.44	7.07	9.35
	Pre-ozonation	31.64	33.83	0.13	3.02	5.75	2.08	16.23	6.62	6.92
	Basin	23.58	23.66	0.09	1.86	2.99	1.08	12.15	5.49	0.34
	Filter	17.69	19.66	0.07	1.12	2.68	0.98	10.08	4.73	11.14
	Finished	14.92	16.51	0.06	0.94	2.49	0.73	8.08	4.21	10.66
R/M	Intake	34.02	37.2	2.03	4.13	6.21	1.32	16.44	7.07	9.35
	Basin	26.64	30.13	1.6	3.08	5.83	1.92	15	2.70	13.10
	Filter	21.01	22.7	1.12	1.84	4.5	1.29	12.6	1.35	8.04
	Finished	19.8	20.3	1.06	1.68	4.38	1.38	10	1.80	2.53
PV	Intake	41.6	40.5	2.9	4.8	4.1	2.2	21.1	5.4	2.3
	Basin	31.6	28.5	2.6	3.1	4.6	2.2	12.4	3.6	10.0
	Filter	18.0	20.4	1.8	2.9	3.3	2.5	8.0	1.9	-14.3
	Finished	16.8	18.3	1.9	2.2	3.0	2.1	7.3	1.8	-8.2

The results show good recovery of the materials to be fractionated given 15% operational tolerance. This provides good foundation for other analytical steps to follow among which are SFS scanning, formation potential testing and GC/liquid-to-liquid extracting.

Figures 30, 31 and 32 show the DOM mass fractions at the R/M, CR and PV plants, respectively, as the fractions flow through the entire treatment train. While it is the general expectation that the TOC in each figure is reduced as the flow exits any of the three treatment plants, from the DOM fractional level, the figures show interesting observations that cannot be possible at the surrogate level. The observations are as follow:

- The hydrophilic base fraction was not very conducive to be removed by coagulation. In fact, figure 30 and 31 show an increase in mass of this fraction across the basin and not so much change across the same in figure 32. While the overall mass cannot be created, this is evidence that there was mass transformation from other fractions as they all experience mass reduction.
- The hydrophobic base fraction was effectively removed by preozonation operation unit as shown in figure 32.

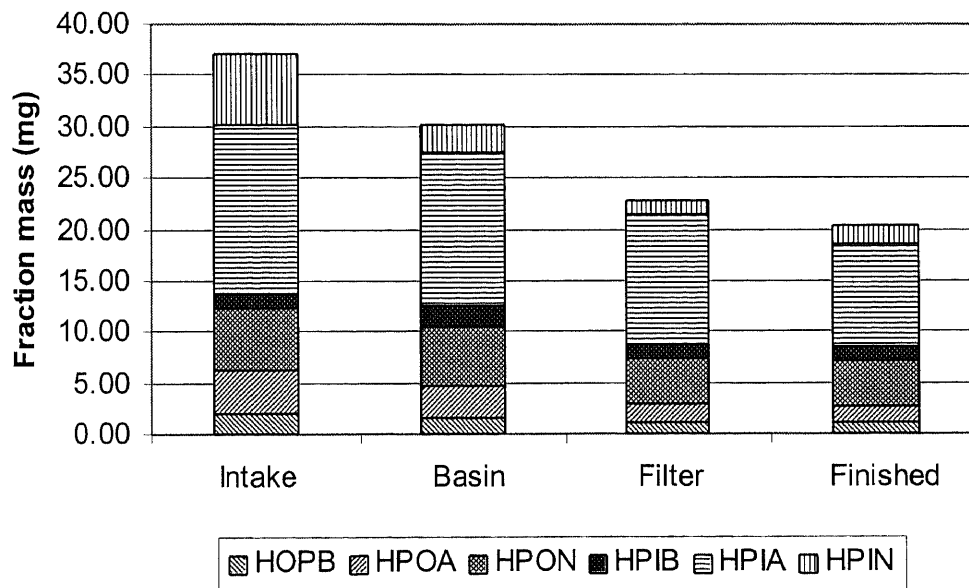


Figure 30 DOM Fraction Mass – RM plant

Figure 31 below shows the mass variation in an ozonation plant. Note the performance, as far as the reduction of organic matter is concerned, is shown to be better with the ozonation process (CR plant) than that of the chlorination process (RM plant). However, while overall TOC may have been removed more in the CR plant, inspection of the finished water shows that it has more certain fractions than the other plant (such as the hydrophobic acid and the hydrophilic neutral fractions). These are among the advantageous features that investigation by finite fraction approach would provide.

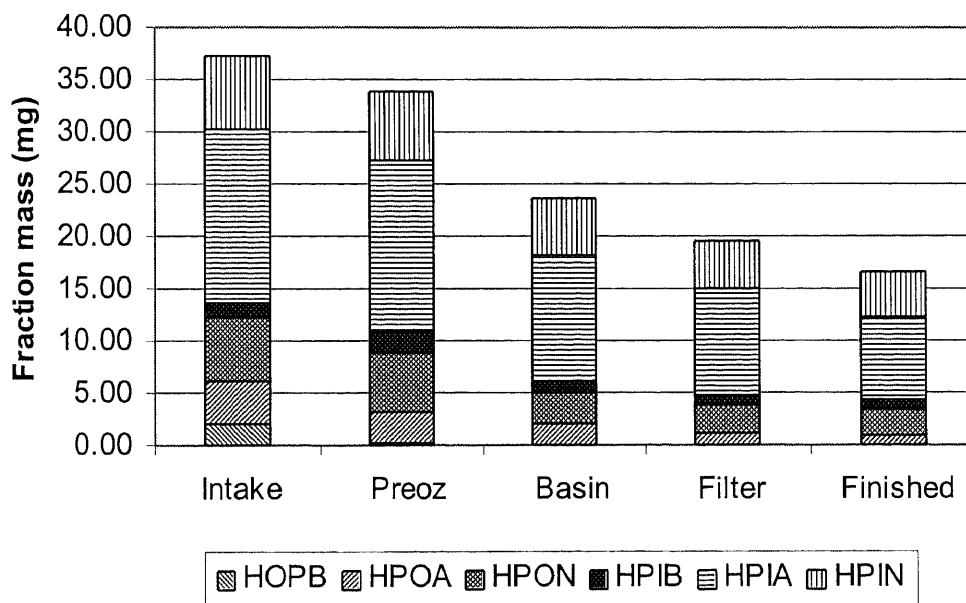


Figure 31 DOM Fraction Mass – CR plant

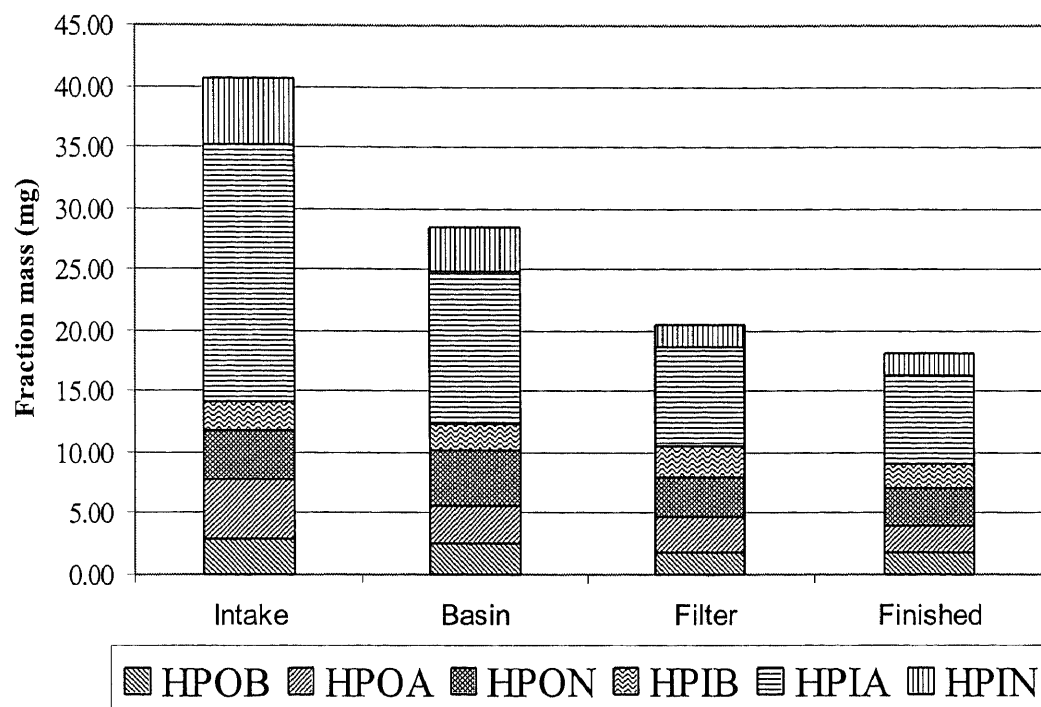


Figure 32 DOM Fraction Mass – PV plant

The hydrophilic acid fraction was most abundant in DOM as evidenced in all three figures above. The distributions of fractions are more clearly shown in figure 33 and 34. This is important because going forward from here the fraction distribution will provide information as to what yields how much formation potential of DBPs as will be seen later on.

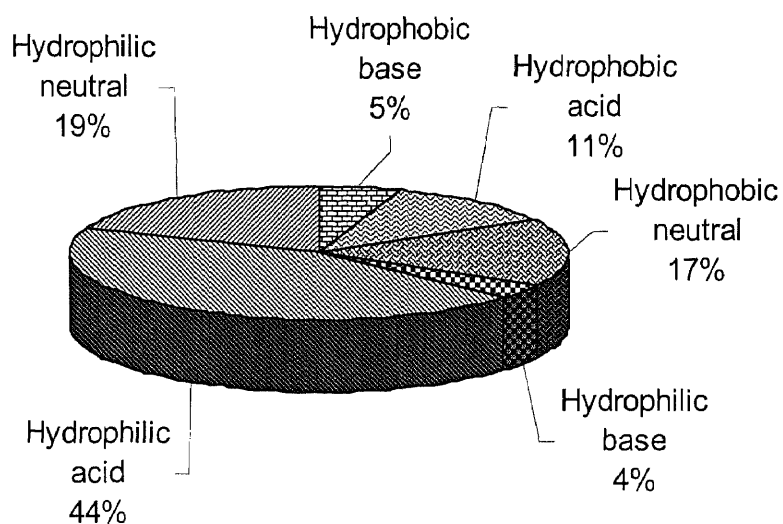


Figure 33 Fraction Distribution in the Common Water Intake of Canal Road and Raritan-Millstone Water treatment plants

The hydrophilic acid is the dominant fraction in two different source waters. More was observed in the Passaic River, however, at the time of sampling than in the Raritan Millstone River.

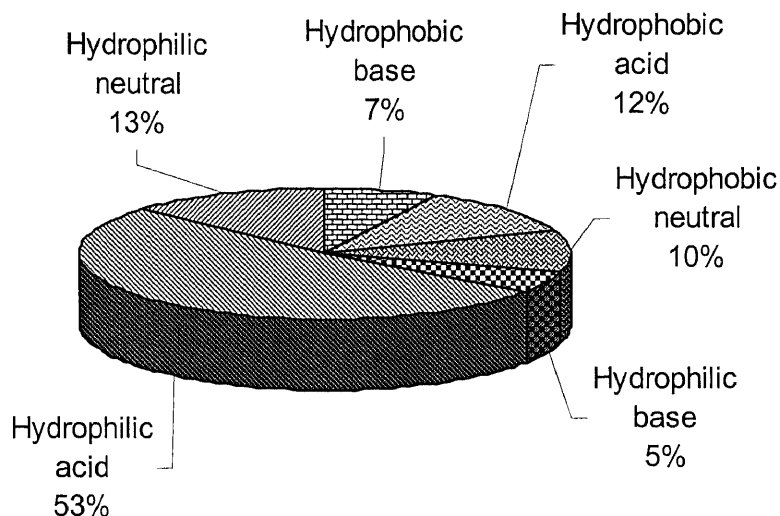


Figure 34 Fraction Distribution in the Intake Water of the PassaicValley Water treatment plant

6.1.1 The Effect of Treatment Processes in the Variation of DOM Mass—a Comparison between Ozonation and Chlorination

The variation of DOM in accordance with source waters is readily understood as different source waters contain different quantity and type of DOM that the WTPs have to operate with. It is important also to know how the mass of DOM fraction varies in different plants employing different disinfection processes. The following section presents such variation by following the DOM fraction from the intake throughout the treatment trains of an ozonation plant (CR) and chlorination plant (RM).

6.1.1.1 The Hydrophobic Base Fraction: Hydrophobic base represented a mass fraction in the range of 0-7% of DOC. A range of 0-22% was reported in other sourcewaters (Aiken *et al.*, 1993; Day *et al.*, 1991; Korshin *et al.*, 1997). The effect of ozonation on the hydrophobic base fraction was significant as shown in figure 35.

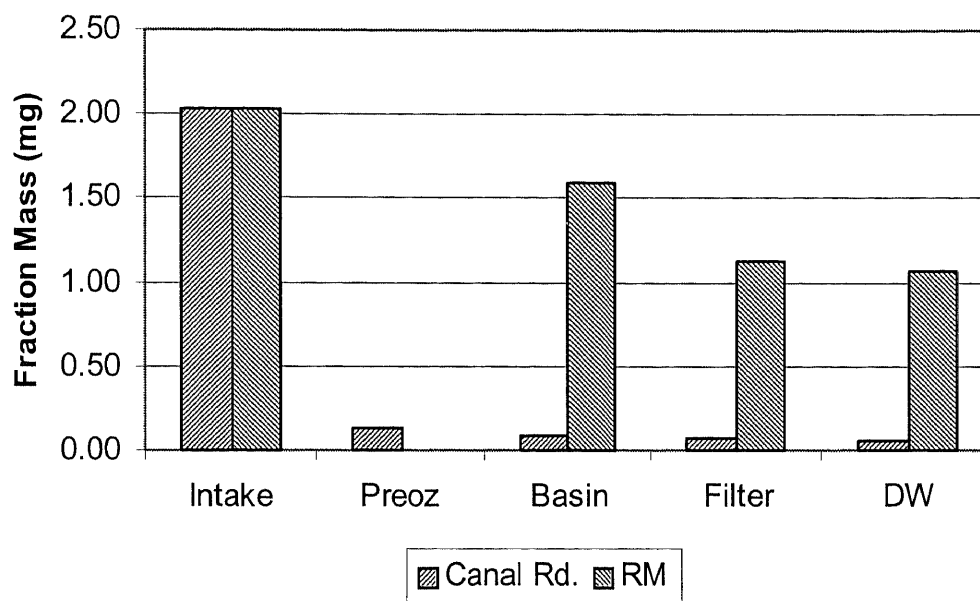


Figure 35 A Comparison of the Variation of the Hydrophobic Base Fraction in the ozonation plant (Canal Rd) and the chlorination plant (RM)

When examining the overall removal at the outlet of the sedimentation basin, this fraction was noticeably reduced (97%) in the case of the Canal Rd water treatment plant, which has pre-ozonation and intermediate ozonation units. As shown in the above figure, most of the reduction (about 94%) was done by the preozonation unit. The benefit of the intermediate ozonation unit is questionable here as far as this fraction of DOM is concerned. The R/M plant, with KMnO_4 pre-oxidation, coagulation and chlorination in sedimentation, had an overall reduction of 48%. Ozonation is known to effectuate physical changes by breaking larger molecular structures into smaller ones. Chemical changes will also result in more oxalic acid type compounds, which contains more oxygenated moieties than are found in nature making the materials more amenable to

biodegradation (Rice, 1980; Amy, 1993; Becker *et al.*, 1996). The hydrophobic base fraction, being a humic substance (as it is widely referred to in the literature), fits well in the criteria for being suitable to oxidation by ozonation. Sharp reduction of this fraction, therefore, represented a mass transformation to hydrophilic fractions as will be discussed later.

Being a humic substance consisting of amino acids, proteic materials, sugars and polysaccharides (Bruchet *et al.*, 1990), the hydrophobic base fraction will react with ozone to produce aldehydes as a class of DBPs (Amy, 1993). This same fraction, when exposed to chlorination, will also produce aldehydes in addition to trihalomethanes (Amy, 1993). Since it is expected that the yield of DBP is a direct function of the organic material, figure 35 indicates that, theoretically, if completely oxidized by chlorination and ozonation, the R/M plant may experience more aldehyde formation than the CR plant. The fraction is otherwise gradually reduced as it flows through other treatment units (i.e. multimedia filtration), as expected.

6.1.1.2 The Hydrophobic Acid Fraction: Hydrophobic acid represented about 8-12% of the DOC by weight at all locations (12% in the raw water). Others have reported a range of 19-68% in raw waters (Aiken *et al.*, 1993; Day *et al.*, 1991; Korshin *et al.*, 1997). Figure 36 shows the reduction of this fraction along the treatment train. The overall reduction again is more pronounced in the ozonation plant (77%) when compared with that of the R/M plant (60%) indicating the influence of both the pre- and intermediate ozonation units as well as the multimedia filter in the removal process. Hydrophobic acid fraction was not observed to have been reduced as much as the

hydrophobic base fraction as discussed in the above section. One of the reasons may be that hydrophobic acid, being a fraction that has the characteristic of soil fulvic, has relatively low comparative concentration to other DOC fractions. In addition, its smaller molecular weight may not have the reaction coordinate sites for targeting by the ozone oxidant.

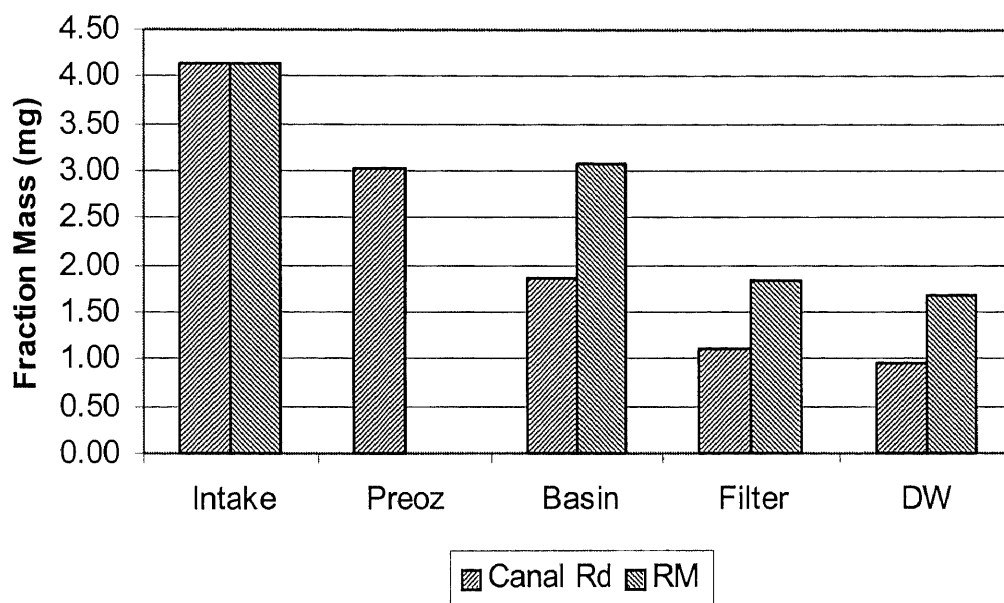


Figure 36 A Comparison of the Variation of the Hydrophobic acid fraction in the ozonation plant (CR) and the chlorination plant (RM)

6.1.1.3 The Hydrophobic Neutral Fraction: Hydrophobic neutral was the most abundant fraction of the hydrophobic substances ranging from 13-22% in all locations (17% in the raw water). This range fell within the raw water range of 0-25% reported by others for sourcewaters (Aiken *et al.*, 1993; Day *et al.*, 1991; Korshin *et al.*, 1997). Hydrophobic neutral is a humic substance in nature, which contains a mixture of

hydrocarbon and carbonyl compounds (Leenheer, 1981). The preozonation unit was not as effective here as compared to how it was with respect to the previous two fractions. A steady but noticeable reduction of this fraction is shown in Figure 37 since conventional unit operations such as coagulation/sedimentation and adsorption are more amenable to the removal of hydrophobic substances than hydrophilic counterparts (Amy, 1993; Reckhow *et al.*, 1984; Jacangelo *et al.*, 1995). The ozonation plant with an intermediate ozonation unit, however, ended up to be more effective in overall removal of this fraction 60% vs. 30% as in the case of the chlorinated plant).

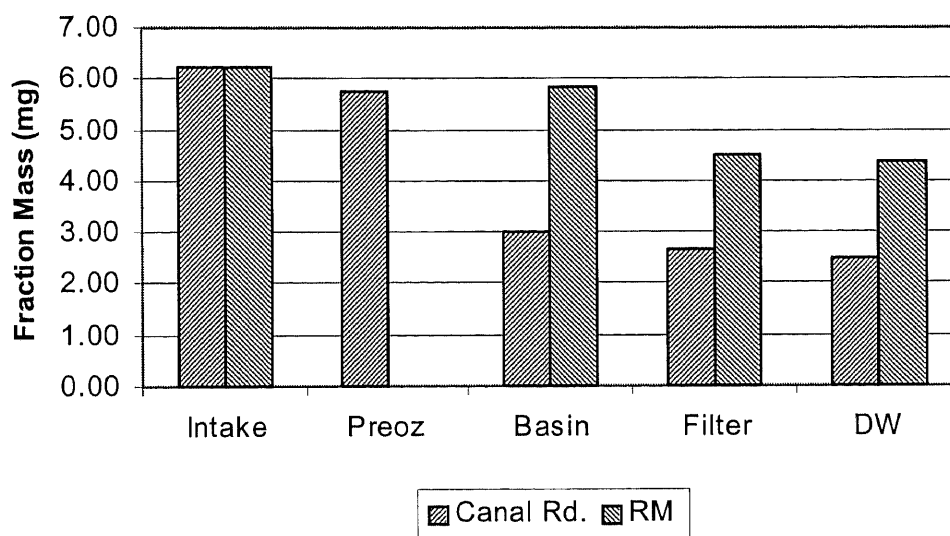


Figure 37 A Comparison of the Variation of the Hydrophobic Neutral Fraction in the Ozone plant (CR) and the Chlorination Plant (RM)

6.1.1.4 The Hydrophilic Base Fraction: Hydrophilic base fraction at all locations ranged from 4-6% of the DOM (4% in the raw water). This range falls within the range of 1.5-10% reported by others for other sourcewaters (Aiken *et al.*, 1993; Day *et al.*, 1991; Korshin *et al.*, 1997). Pre-ozonation increased the hydrophilic base fraction as shown in

figure 8. The increase of 58% is believed to be the transformation of mass from the hydrophobic base fraction (figure 35). The breakup of mass into smaller molecular sizes and the transformation of materials from non-biodegradable to biodegradable (by the ozonation process) have been well established by others (Rice, 1980; Amy, 1993; Becker et. al., 1996). Figure 38 shows that, for the ozonation plant, the increase of the hydrophilic base fraction mass following ozone unit operations (both pre- and intermediate) was immediately followed by a comparable decrease following coagulation/sedimentation and filtration.

Overall, figure 38 shows that, as far as this fraction is concerned, the ozonation plant has low effectiveness in oxidizing the material. However, the chlorinated plant was not at all effective in treating this fraction. The micro-flocculation in the ozonation plant may have played an important role with regard to the observed performance of the plant. Micro-flocculation or pre-flocculation is a phenomenon usually observed after the preozonation unit where condition has been seen to promote further flocculation in the downstream coagulation/sedimentation chambers)

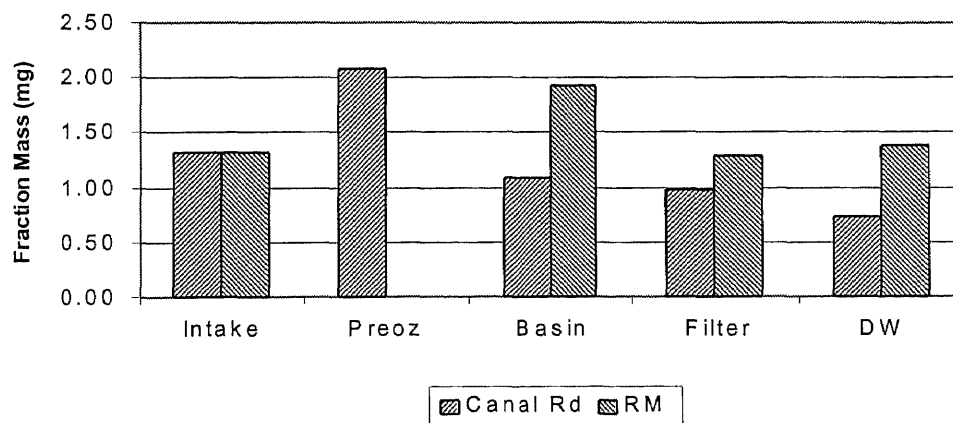


Figure 38 A comparison of the variation of the hydrophilic base fraction in the ozonation plant (CR) and the chlorination plant (RM)

6.1.1.5 The Hydrophilic Acid Fraction: This fraction was the most abundant and was found to be in the range of 44 to 55% of the DOC at all locations (48% in the raw water). It has been reported by others to be in the range of 8 to 50% in other sourcewaters (Aiken *et al.*, 1993; Day *et al.*, 1991; Korshin *et al.*, 1997). The comparison, as shown in Figure 39, does not indicate any significant difference between the two plants on the removal of this fraction. The overall reduction in the ozonation plant was about 50% while that of the chlorination plant was about 40%. The ozonation plant fares better in this case perhaps due to the GAC-containing filter, which also exhibits biofiltration capacity as discussed earlier in the Water Treatment Processes section. This was a confirmation of earlier study (Bose, 1994) which found that hydrophilic acid was the least among the DOM fractions that form carboxyl group in the presence of the oxidant, ozone.

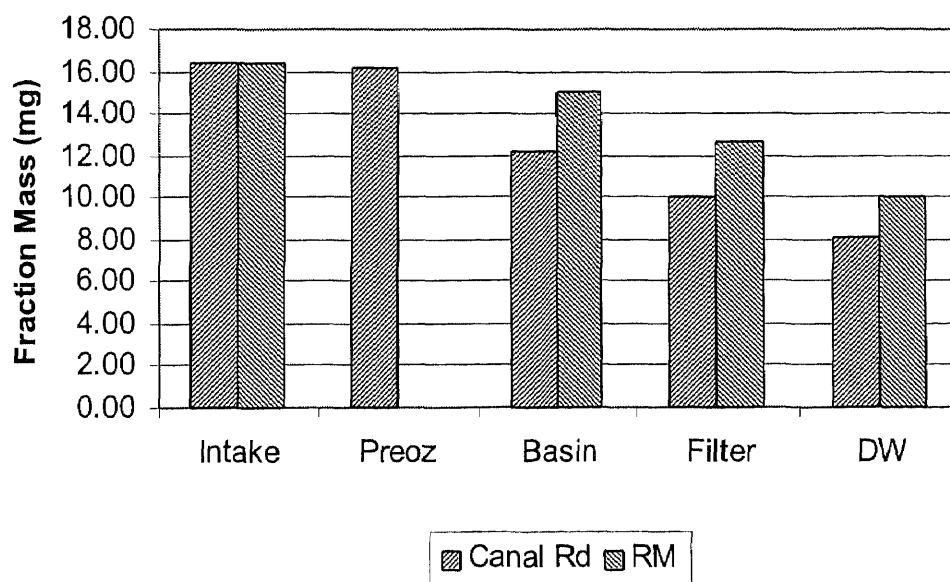


Figure 39 A Comparison of the Variation of the Hydrophilic Acid Fraction in the Ozonation Plant (CR) and the Chlorination Plant (RM)

6.1.1.6 The Hydrophilic Neutral Fraction: This fraction represented a range from 9 to 25% of the DOC (21% in the raw water). A range of 1-35% was reported for other sourcewaters by others (Aiken *et al.*, 1993; Day *et al.*, 1991; Korshin *et al.*, 1997). Figure 40 shows that the CR plant with pre- and intermediate ozonation units was not as effective in treating this fraction as compared to the conventional chlorinated R/M treatment plant (an overall reduction of 40% in the CR plant vs. 75% in the R/M plant). As in the case of the hydrophilic acid fraction, ozonation reactivity of this fraction was not significant (Bose, 1994). It is important to note that the hydrophilic neutral fraction whose content is made up of polysaccharides (Tipson, 1968; Bruchet *et al.*, 1987) is not expected to be as problematic a DBP precursor as other fractions.

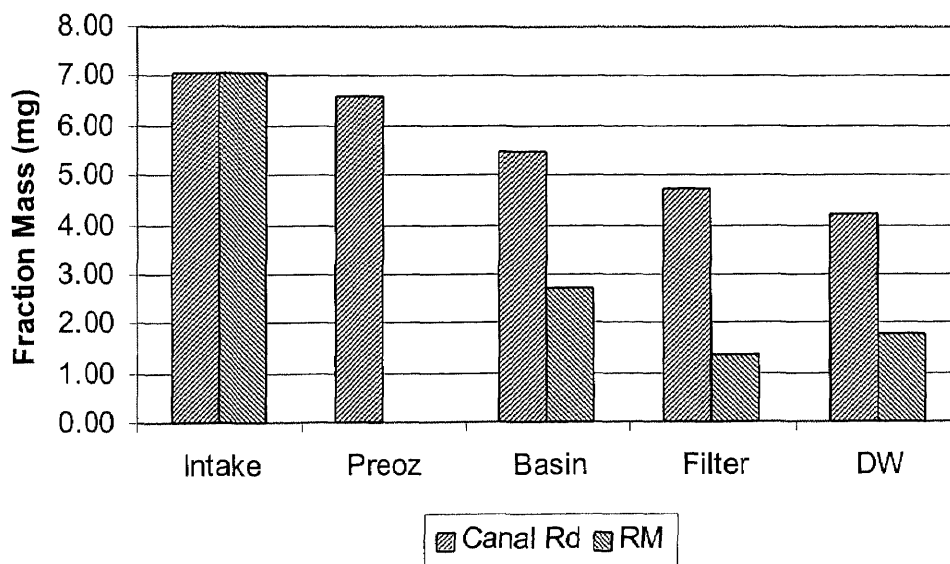


Figure 40 A Comparison of the Variation of the Hydrophilic Neutral fraction in the ozonation plant (CR) and the chlorination plant (RM)

Table 16 Summary of the Hydrophobic Substances

Plants	Hydrophobic Fractions (mg)			Total (mg)
	Base	Acid	Neutral	
CR Plant Before Filter	0.09	1.86	2.99	4.94
CR Plant After Filter	0.07	1.12	2.68	3.87
R/M Plant Before Filter	1.60	3.08	5.83	10.51
R/M Plant After Filter	1.12	1.84	4.50	7.46

Table 17 Summary of The Hydrophilic Substances

Plants	Hydrophilic Fractions (mg)			Total (mg)
	Base	Acid	Neutral	
CR Plant Before Filter	1.08	12.15	5.49	18.72
CR Plant After Filter	0.98	10.08	4.73	15.79
R/M Plant Before Filter	1.92	15.00	2.70	19.62
R/M Plant After Filter	1.29	12.60	1.35	15.24

It is interesting to compare data in tables 16 and 17 above with regards to the effectiveness and functionality of the filtration units in these two plants. While it is expected that both plants would show filtration to work more effectively with overall hydrophobic substances than the hydrophilic ones, it is surprising to see the filtration unit in the chlorination plant to be more effective with regards to the hydrophilic substances. The reverse would be the expectation since the multimedia filtration unit in the ozonation plant was supposed to also function as a biofiltration unit. The lethargy in bioactivity of the filter could only be conjectured although the low ozone-to-DOC ratio could make it a credible suspicion.

6.1.2 Aggregate vs. Fractionated DOM

While aggregate (or pre-fractionated) DOC data from Table 18 shows moderate difference between the ozonation plant and the conventional plant, the differences are much more noticeable when the comparison is based on the DOM fractions. Because each fraction is made up of different organic compounds which react quite differently in producing DBPs, the aggregate DOC as measured by the persulfate/UV oxidation method is, as a result, quite limited in predicting DBP formation potential and treatment effectiveness of the DBP precursors.

Table 18 Overall DOC and Precursor Removal

Parameter	Canal Road (%)	Raritan-Millstone (%)	Passaic Valley (%)
Aggregate DOC	56	42	60
Hydrophobic base fraction	97	48	34
Hydrophobic acid fraction	77	60	54
Hydrophobic neutral fraction	60	30	27
Hydrophilic base fraction	45	(5)	4.5
Hydrophilic acid fraction	51	39	65
Hydrophilic neutral fraction	40	75	67

6.2 The Variation of DBP FP along the Treatment Train

The mass of the isolated fractions, being varied through the treatment train with the exception of the hydrophilic base fraction, has discussed in section 6.1 above. With that in the background, the following section presents the data, and the discussion, of the resultant DPB FP of each fraction as it is subjected to the different unit operations as they flow through the treatment trains. The discussion is important in that it provides information into the effectiveness of the various unit operations in the plant as they are related to the removal of certain targeted fractions.

6.2.1 The Effect of Treatment Processes

It is intuitive to understand that the variation of DBP FP is influenced by the type of disinfection process being employed and the source water that the flow is being drawn from. The section that follows takes into account the effect of different disinfection processes by comparing DBP FP in an ozonation plant with that in a chlorination plant.

6.2.1.1 The Hydrophobic Base Fraction: The variations of the formation potential of THMs and HAAs of this fraction are shown in figure 43 and 44 below.

Comparatively, the ozonation plant with post chlorination has a larger overall reduction of this category of DBP FP— 78% vs 66% in chlorination plant.

The better performance of the CR plant may be explained from the two design features of the plant. One is ozonation. Ozonation is known to effectuate physical changes by breaking larger molecular structures into smaller ones. Chemical changes will also result in more oxalic acid type compounds, which contain more oxygenated molecules than are

found in nature making the materials more amenable to biodegradation (Rice, 1980; Amy, 1993; Becker *et al.*, 1996). Following the intermediate ozonation unit, the ozonation plant has a GAC-containing filter, which also performs biofiltration. Micro-flocculation in the ozonation plant may have played an important role with regard to the observed performance of the plant. Micro-flocculation or pre-flocculation is a phenomenon usually observed after the prec ozonation unit where condition has been seen to promote more effective flocculation in the downstream coagulation/sedimentation chambers). It is the combination of ozonation, biofiltration and microfloculation that are believed to be responsible for the enhancement of the THM disinfection byproduct precursor removal.

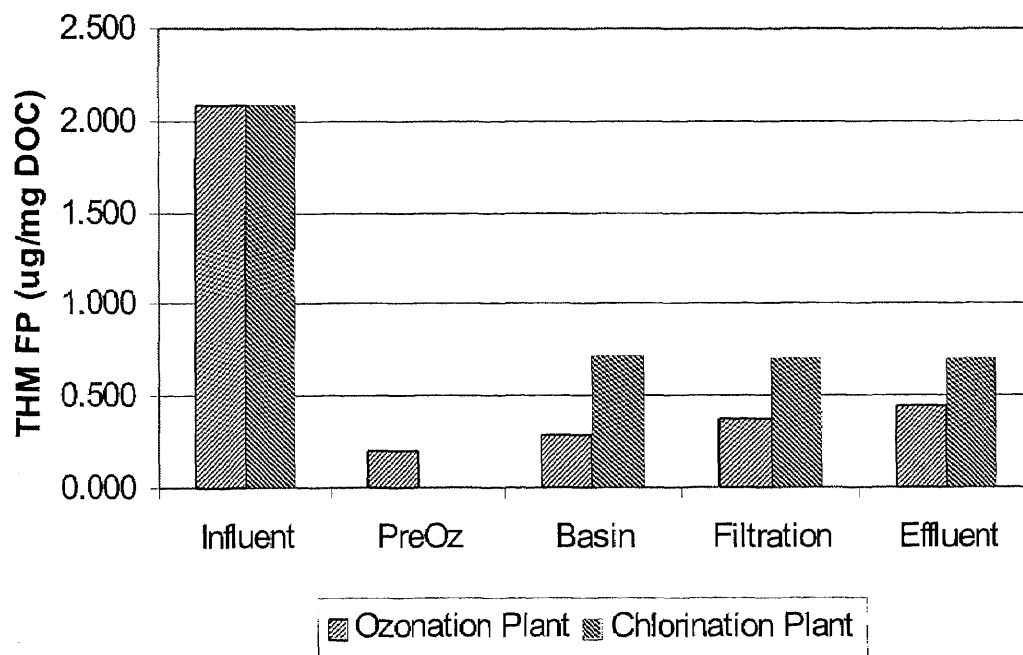


Figure 41 Variation of the THM FP of the hydrophobic base fraction along the treatment train (ozonation plant vs. chlorination)

With respect to HAAs, since conventional unit operations such as coagulation/sedimentation and adsorption are more amenable to the removal of hydrophobic substances than the hydrophilic counterparts (Amy, 1993; Reckhow *et al.*, 1984; Jacangelo *et al.*, 1995), a comparison of figure 43 and 44 from the standpoint of the overall reduction suggests that, as far as the hydrophobic base fraction is concerned, HAA DBP precursors are more hydrophobic than the THM DBP precursors.

Figure 44 also indicates better performance by the chlorination in the overall HAA DBP FP reduction than the ozonation plant (82% vs. 71%).

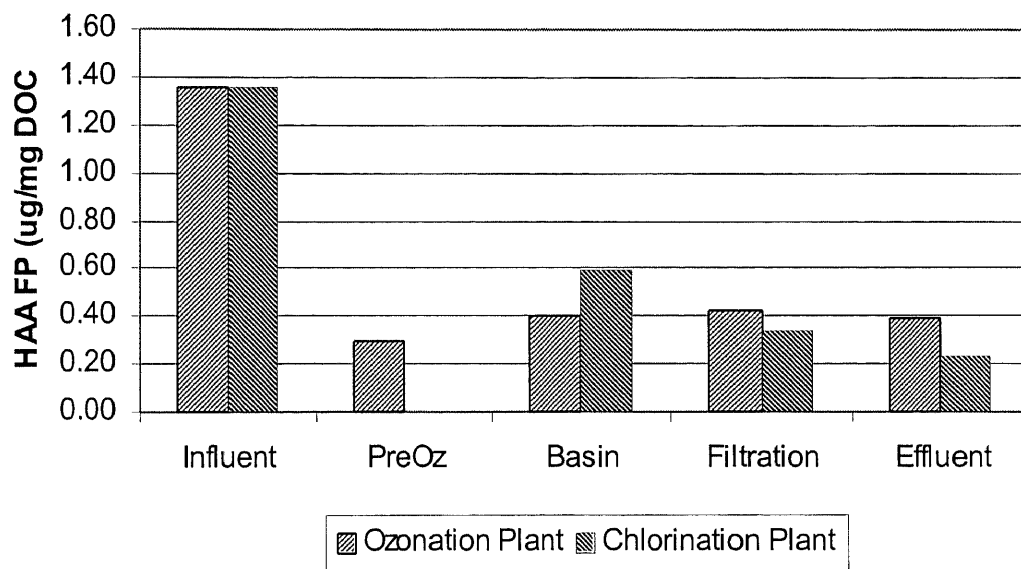


Figure 42 Variation of the HAA FP of the hydrophobic base fraction along the treatment train (ozonation plant vs. chlorination).

6.2.1.2 The Hydrophobic Acid Fraction: The variations of this fraction with respect to the formation potential of THMs and HAAs are shown in figure 45 and 46 below.

Results show that the ozonation plant again does it better in reducing the THM FP caused by this fraction (65% vs. 55%). The fraction is more amenable be reduced by the

coagulation/sedimentation processes than filtration process. The opposite is true as shown by figure 44 with regard to the HAAs FP (84% chlorination plant vs 71% ozonation plant).

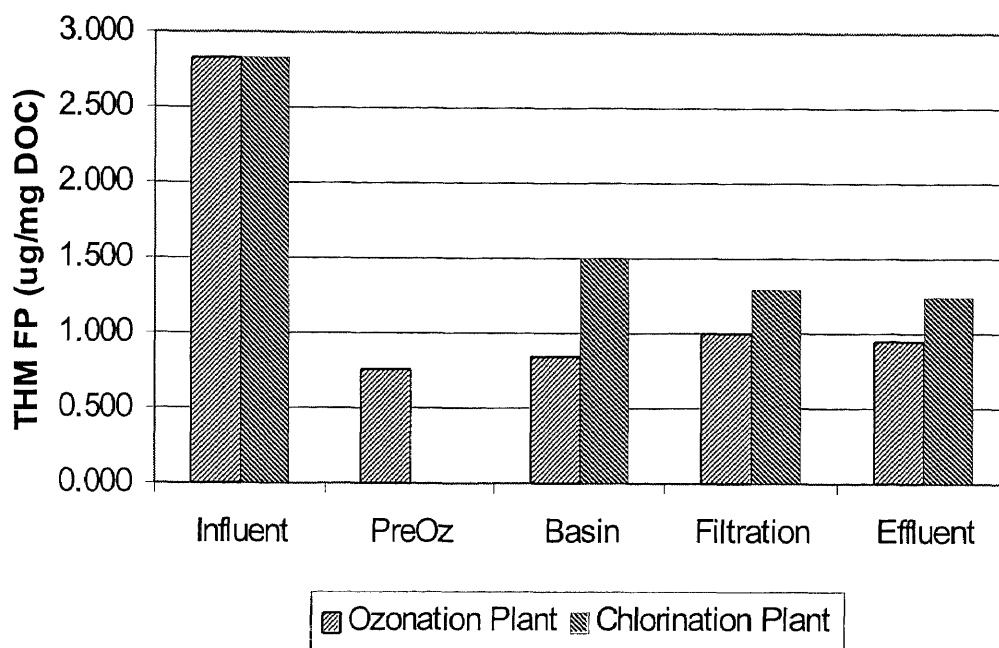


Figure 43 Variation of the THM FP of the hydrophobic acid fraction along the treatment train__ a comparison of ozonation against chlorination (ozonation vs. chlorination plant)

Ozonation as a disinfection process works more effectively in reducing the potential of formation of trihalomethanes than the chlorination plant. Most of the reduction is shown following the preozonation unit.

The chlorination plant is shown below to handle the precursor of HAA FP more effectively. Most of the reduction was by coagulation and sedimentation.

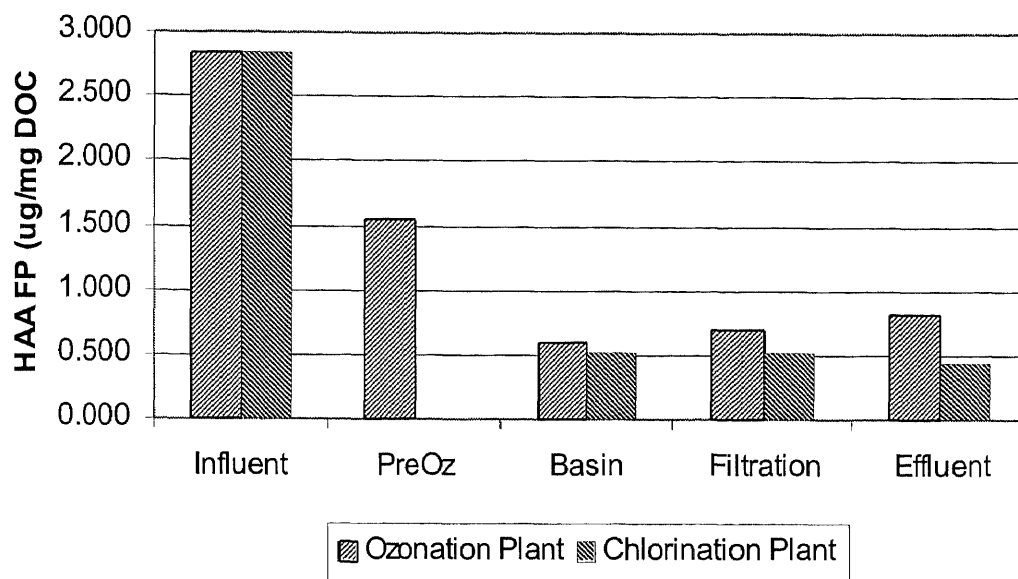


Figure 44 Variation of the HAA FP of Hydrophobic Acid Fraction along the Treatment train__ a Comparison of Ozonation against chlorination (ozonation vs. chlorination plant)

6.2.1.3 The Hydrophobic Neutral Fraction

The hydrophobic neutral fraction is influenced by the disinfection processes in different ways depending on the type of precursor as in the case of the hydrophobic acid fraction.

Preozonation plant handles the THM precursor better than the chlorination plant. The sedimentation basin works well in complement with the preozonation unit to bring about the better performance.

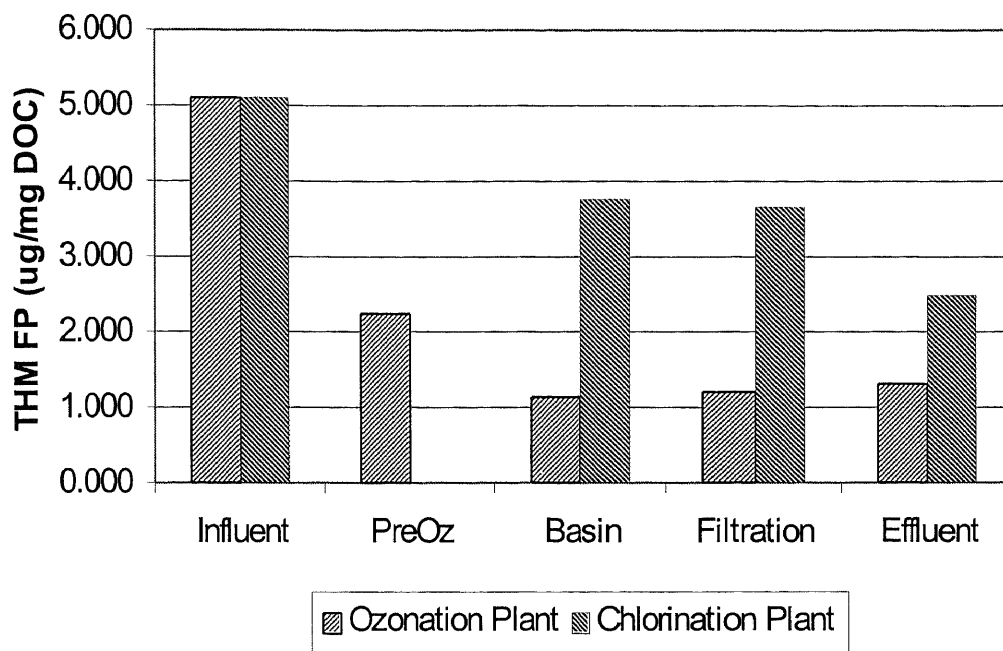


Figure 45 Variation of the THM FP of the Hydrophobic Neutral Fraction along the Treatment train (Ozonation versus Chlorination)

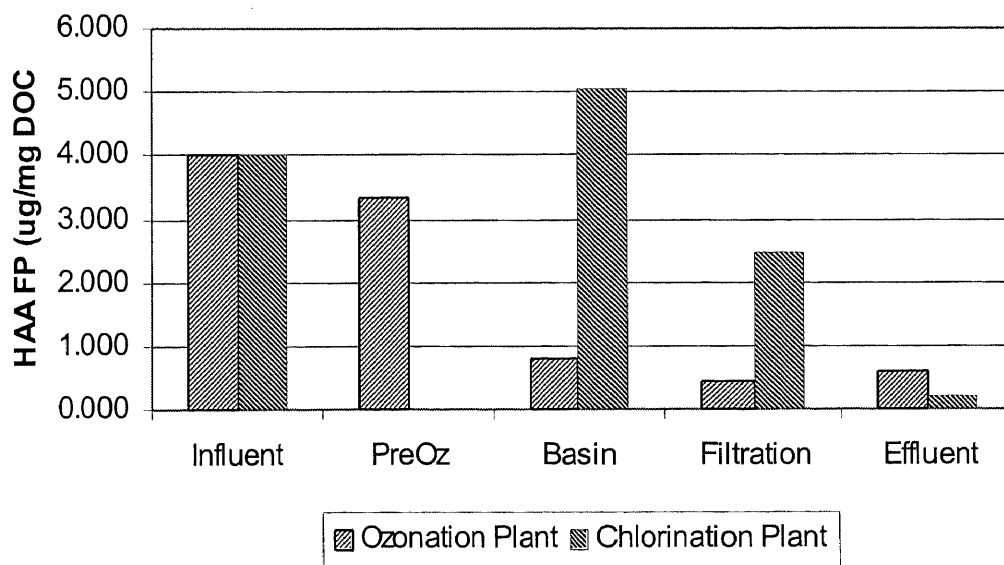


Figure 46 Variation of the HAA FP of the Hydrophobic Neutral fraction along the treatment train (ozonation versus chlorination)

6.2.1.4 The Hydrophilic Base Fraction: The variations of the formation potential of this fraction along the treatment train are shown in figure 47 and 48 below for THMs and HAAs, respectively.

Data show that the chlorination process was more effective in treating this fraction. The observed post-filtration increase in the DBP FP in the CR plant was believed to have been caused by the intermediate ozonation unit operation that was discussed in section 6.1.2.4 above.

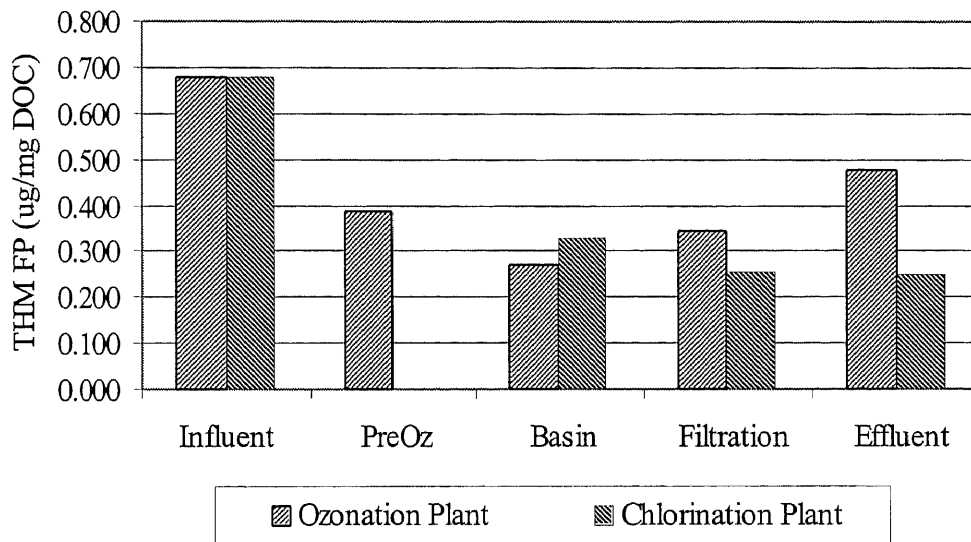


Figure 47 Variations concerning the THM FP of the hydrophilic base fraction along the treatment train.

In a conventional chlorination WTP, the precursor of HAA was seen to gradually decrease as it would be expected. As shown below, the coagulation/sedimentation unit operations contributed most in the overall removal of the type of precursor. The trend

continue to hold true in that the chlorination disinfection process is more conducive to the treatment of the HAA FP issue than the ozonation plant.

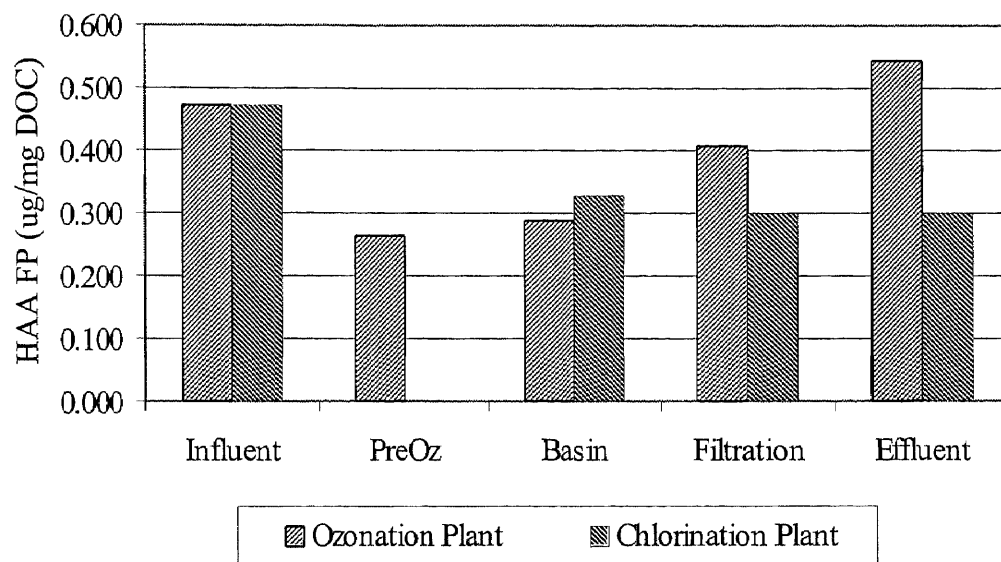


Figure 48 Variation of the HAA FP of the hydrophilic base fraction along the treatment train__ a comparison of ozonation against chlorination

6.2.1.5 The Hydrophilic Acid Fraction: Not only is the hydrophilic acid fraction the most reactive fraction when exposed to chlorine, it is the most problematic precursor in the formation of THMs. For the formation of HAAs, it is the second most problematic precursor.

Preozonation by itself wasn't very effective in reducing the FP of hydrophilic acid DBPs. However, it does promote conditions that make the coagulation process very effective. Again, the benefit of micro-flocculation is being observed here as the main benefit of preozonation. The overall reduction of THM FP was about 30% after going through the treatment train. Without ozonation (both pre and intermediate stages), the

R/M plant showed an overall reduction of about 20%. For either plant, this is relatively low as compared to other fractions in the humic or hydrophobic category that was discussed previously.

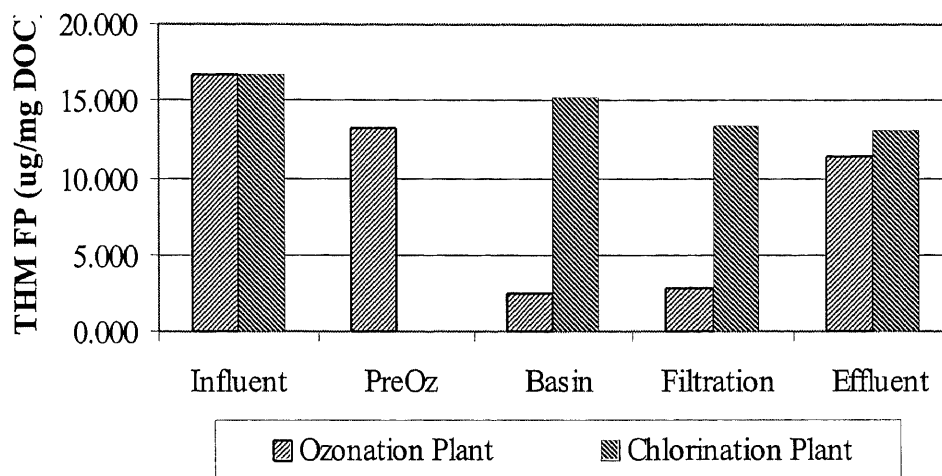


Figure 49 Variation of the THM FP of the Hydrophilic Acid Fraction along the Treatment Train__ a Comparison of Ozonation against Chlorination

For HAA FP as shown in figure 50, although the difference is small here (about 4%) between the two plants, the pattern seems to be holding that the chlorination plant can effectuate the reduction of this fraction better than the ozonation plant.

The problem of HAA as a disinfection by product caused by the hydrophilic acid fraction does not seem to be so serious since it can be quite readily removed (figure 52). THM FP caused by this fraction, however, is a different issue that remains to be a challenge as to how to remove it better.

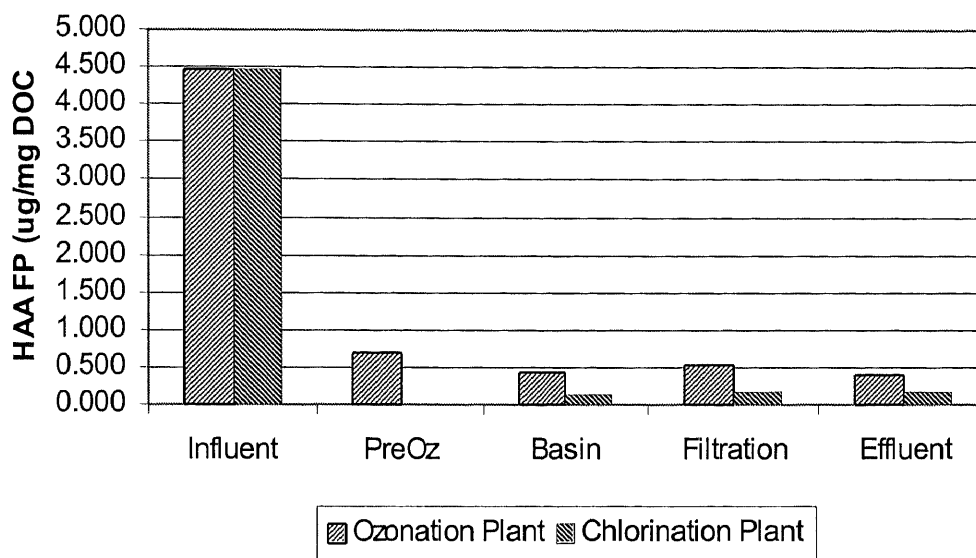


Figure 50 Variation of the HAA FP of the Hydrophilic Acid Fraction along the Treatment Train__a Comparison of Ozonation against Chlorination

6.2.1.6 The Hydrophilic Neutral Fraction: Ozonation does seem to be effective in reducing the FP of hydrophilic neutral precursor as far as THMs and HANs are concerned. While the chlorination plant shows better performance with regard to the HAA DBP class, the hydrophilic neutral fraction does not contribute significantly in the formation of DBPs whether in the THMs or HAAs categories. The reason for this is this fraction is primarily made up of polysaccharides (Tipson, 1968) that are not very reactive with chlorination (Mallevalle, 1993).

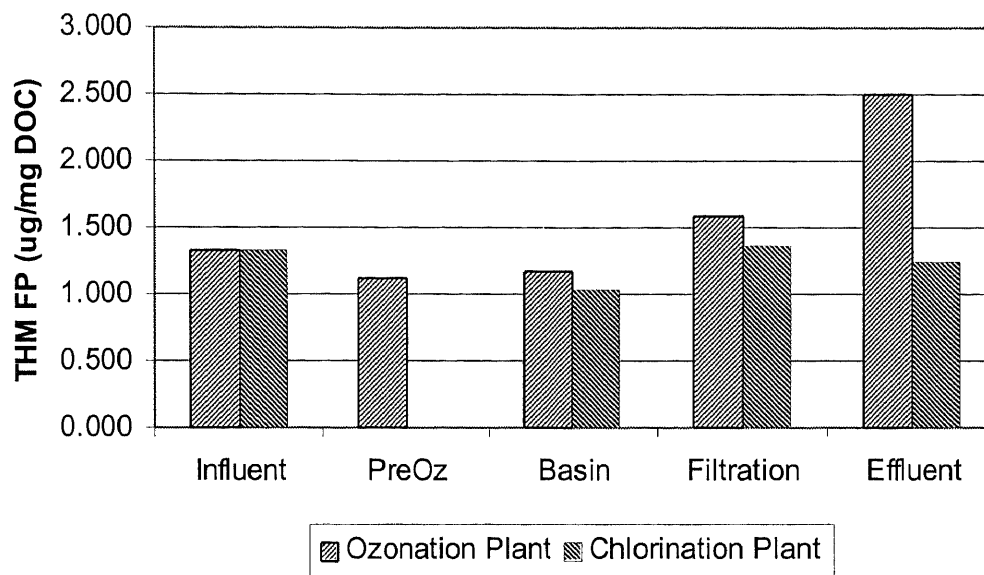


Figure 51 Variation of the THM FP of the Hydrophilic Neutral Fraction along the Treatment Train__ a Comparison of Ozonation against Chlorination

Consistent with earlier results in the study of fraction mass variation (figure 30 and 31), the formation potential of this fraction as shown in the above figure has also experienced an increased here in the effluent. The intermediate ozonation is believed to be the contributor toward this occurrence as it has been known to cause material transformation from humic to nonhumic substance or from hydrophobic to hydrophilic status (Rice, 1980; Amy, 1993; Becker *et al.*, 1996).

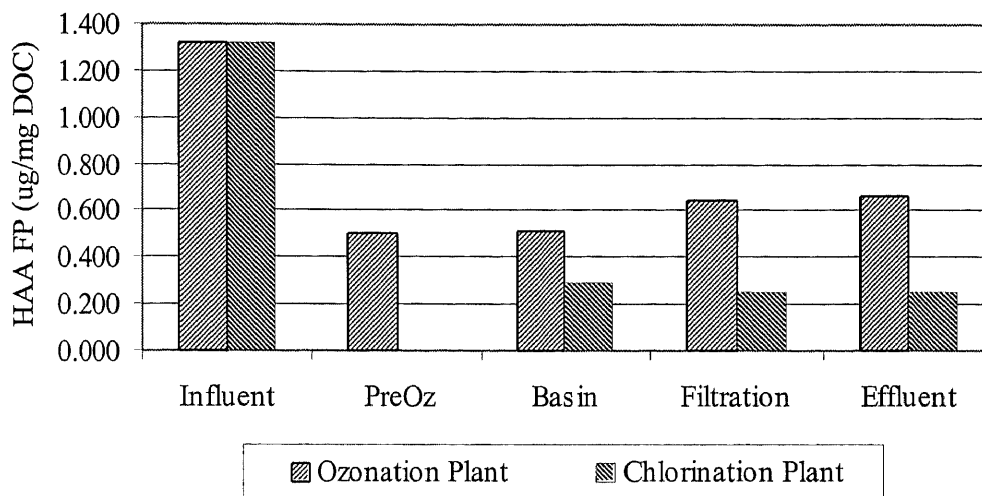


Figure 52 Variation of the HAA FP of the Hydrophilic Neutral Fraction along the Treatment Train__ a Comparison of Ozonation against Chlorination

6.3 Validation of Results

The following tables and figures show predicted values from the SFS toolkit and the actual values as measured by the TOC analyzer. Method validations were carried out at all of the unit operations along the treatment trains in all three WTPs. As shown below, all predicted values compared well with the observed values at 11 out of 12 sample points.

6.3.1 Validation Using Influent Water Sample

The procedures that were used for the validation results were presented in details in section 5.1.3

Table 19. Summary of validated results. Samples from influent of the Canal Road water treatment plant. Values are in mg/L (5/21/1998).

Fraction	Concentration (mg/L)	
	Predicted	Observed
HPOB	0.4	0.5
HPOA	0.1	0.2
HPON	0.6	0.7
HPIB	2.0	1.8
HPIA	0.1	0.2
HPIN	0.8	0.8

Results tabulated here in table 19 and figure 53 show very good correlation of the predicted value of what was observed. The coefficient of correlation of 0.99 was excellent as it was confirmed by the 5% and 1% levels of significance. These two values of 5% and 1% level of significance are 0.811 and 0.917. The coefficient of correlation of 0.99 is greater than both of these two values (Martin Sternstein, 1994).

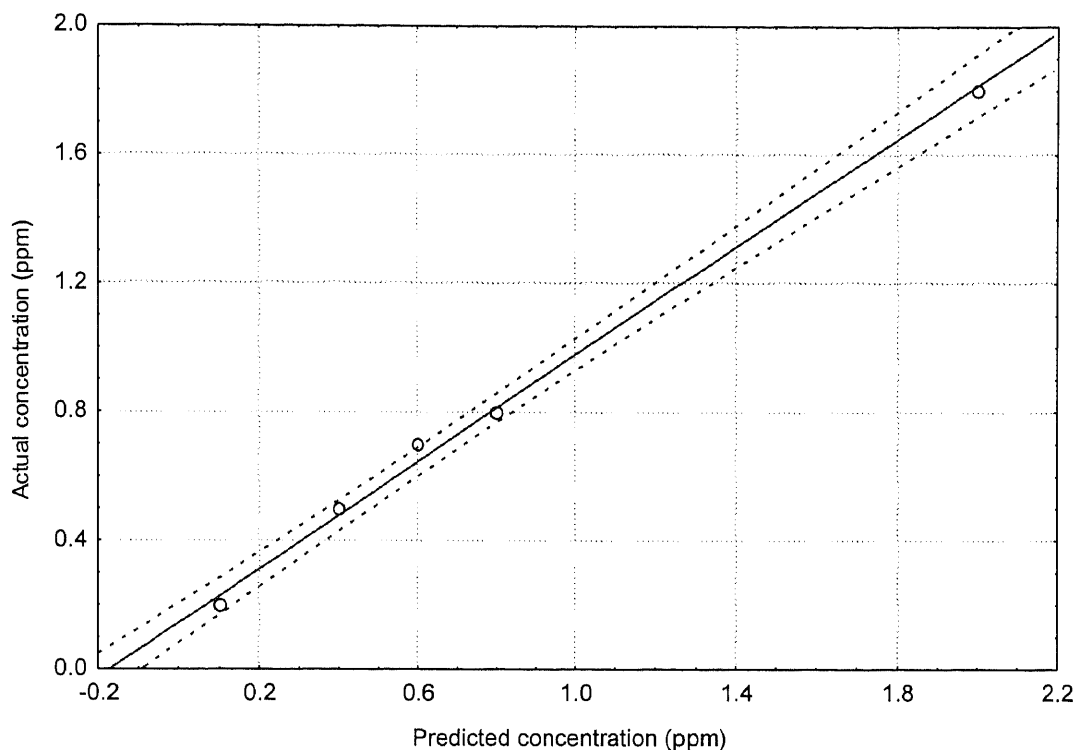


Figure 53 Predicted Concentrations As Compared to Actual Concentration. Influent Water Sample of the CR plant (May 21, 1998). Results analyzed with 95% confidence level. Coefficient of Correlation of 0.99. $y = 0.84(x) + 0.14$ The limits of the Correlation are 0.1 to 2 ppm

Method validation was carried using influent water that was drawn from a different source water serving the Passaic Valley water treatment plant. The results are as follow (table 20 and figure 54):

Table 20 Summary of Validated Results. Samples from Influent of the Passaic Valley Water Treatment Plant. Values are in mg/L (4/28/1998)

Fraction	Concentration (mg/L)	
	Predicted	Observed
HPOB	0.5	0.5
HPOA	0.8	0.3
HPON	0.5	0.5
HPIB	2.4	2.3
HPIA	0.3	0.3
HPIN	0.5	0.6

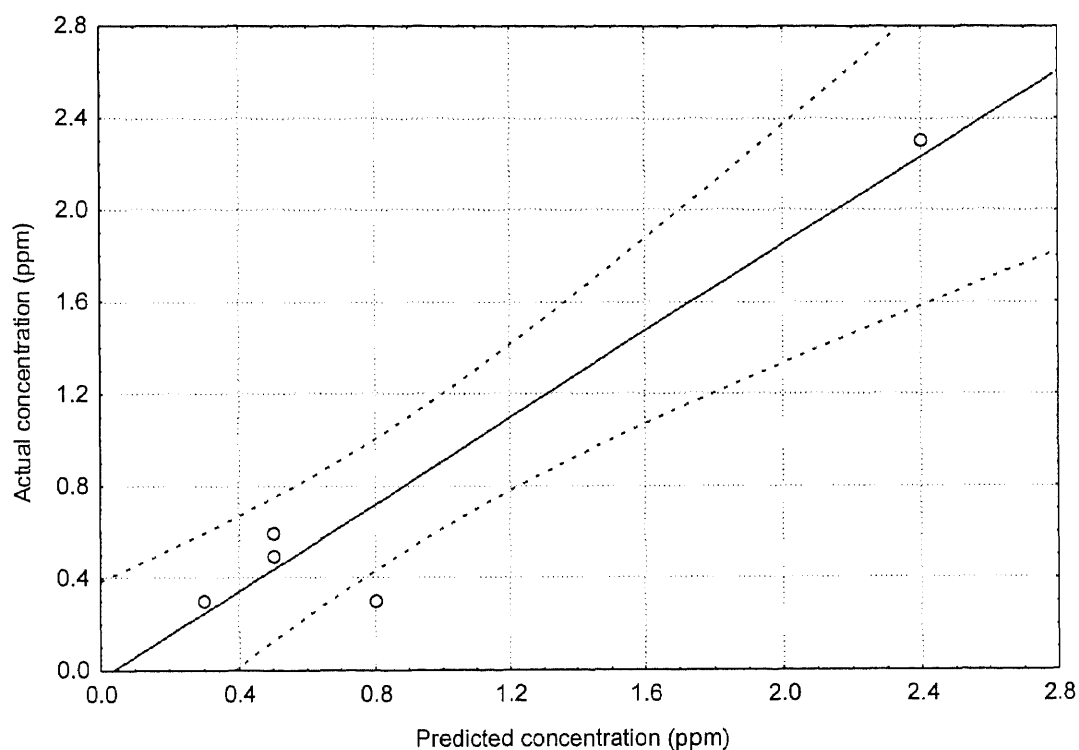


Figure 54 Predicted Concentrations As Compared to Actual Concentration. Influent Water Sample of the PV Plant (April 28, 1998). Results analyzed with 95% confidence level. Coefficient of Correlation of 0.96. $y = 0.94(x) - 0.04$ The Limits of the Correlation are 0.3 to 2.4 ppm

The relationship as shown above again has very good correlation. As R of 0.96 is compared favorably with the two level of significance test of 5% and 1%, which

calculated at 0.811 and 0.917 based on the degree of freedom of 6 less 2 (Martin Sternstein, 1994).

For each of the source waters mentioned above, SFS toolkit arrived at the list of results above in less than 60 minutes which was inclusive of fluorescence scanning time. This is phenomenal as compared to length of time by the current analytical methods if the same results are to be produced.

Although most of the information regarding the DOM's DBP precursor removal are desired in the source water and at the intake to the treatment plants, the following validations were undertaken for the rest of the plant's treatment locations. This is to test the flexibility of the SFS toolkit when its influent-related database is used elsewhere in the plant.

6.3.2 Validation Using Water Samples from the Sedimentation Basins

Validating using the water coming out of the sedimentation basin at the Passaic Valley plant (table 21 and figure 55):

Table 21 Summary of Validated Results. Samples from Sedimentation Basin of the Passaic Valley Water Treatment Plant. Values are in mg/L (4/28/1998)

Fraction	Concentration (mg/L)	
	Predicted	Observed
HPOB	0.3	0.3
HPOA	0.2	0.3
HPON	0.3	0.5
HPIB	0.2	0.2
HPIA	1.8	1.4
HPIN	0.9	0.4

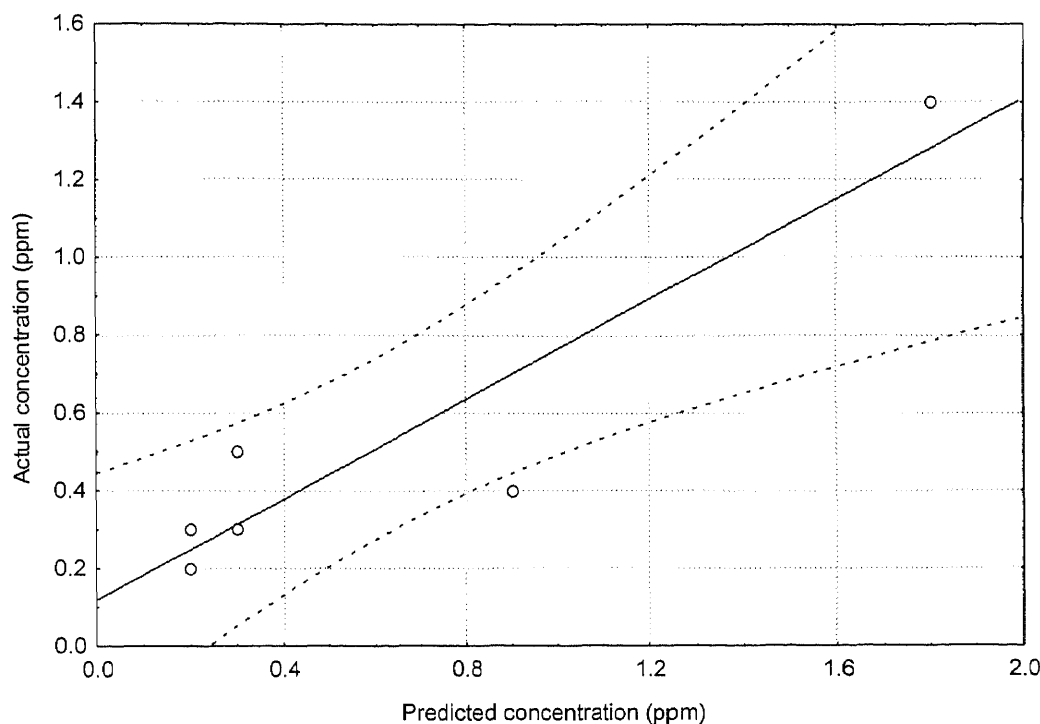


Figure 55 Predicted Concentrations As Compared to Actual Concentration. Sedimentation Water Sample of the PV Plant (April 28, 1998). Results analyzed with 95% Confidence Level. Coefficient of Correlation of 0.92. $y = 0.63(x) + 0.12$ The Limits of the Correlation are 0.2 to 2 ppm

As indicated by the coefficient of correlation of 0.92, applying the two tests of significant levels as before, the correlation is strong. The same discussion and conclusion apply to the validation using the sedimentation basin of the Canal Road as shown below (table 22 and figure 56):

Table 22 Summary of Validated Results. Samples from Sedimentation Basin of the Canal Road Water Treatment Plant. Values are in mg/L (5/21/1998)

Fraction	Concentration (mg/L)	
	Predicted	Observed
HPOB	0.2	0.01
HPOA	0.2	0.2
HPON	0.3	0.3
HPIB	0.1	0.1
HPIA	1.3	1.4
HPIN	0.3	0.6

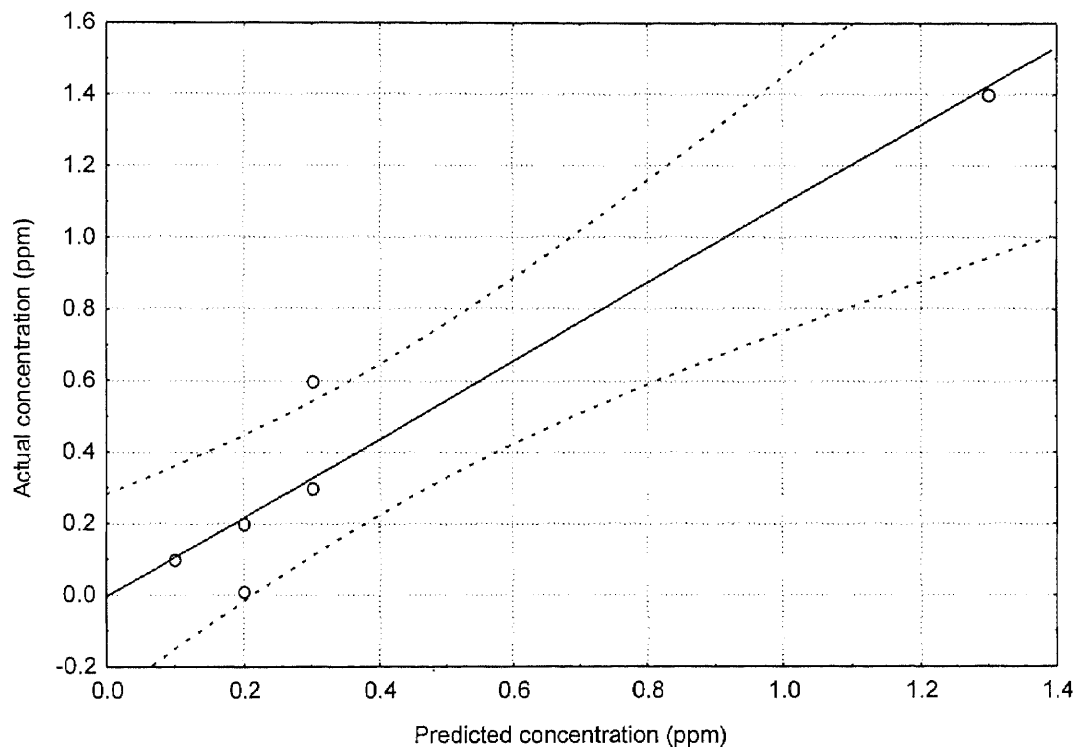


Figure 56 Predicted Concentrations As Compared to Actual Concentration. Sedimentation Water Sample of the CR plant (May 21, 1998). Results Analyzed with 95% Confidence Level. Coefficient of Correlation of 0.95. $y = 1.10(x) - 0.004$ The Limits of the Correlation are 0.1 to 1.5 ppm

The following continues with the results validation using the sedimentation basin of the Raritan Millstone water treatment plant (table 23 and figure 57):

Table 23 Summary of Validated Results. Samples from Sedimentation Basin of the Raritan Millstone Water Treatment Plant. Values are in mg/L (5/21/1998)

Fraction	Concentration (mg/L)	
	Predicted	Observed
HPOB	0.1	0.2
HPOA	0.2	0.3
HPON	0.3	0.6
HPIB	0.1	0.2
HPIA	1.2	1.7
HPIN	0.3	0.3

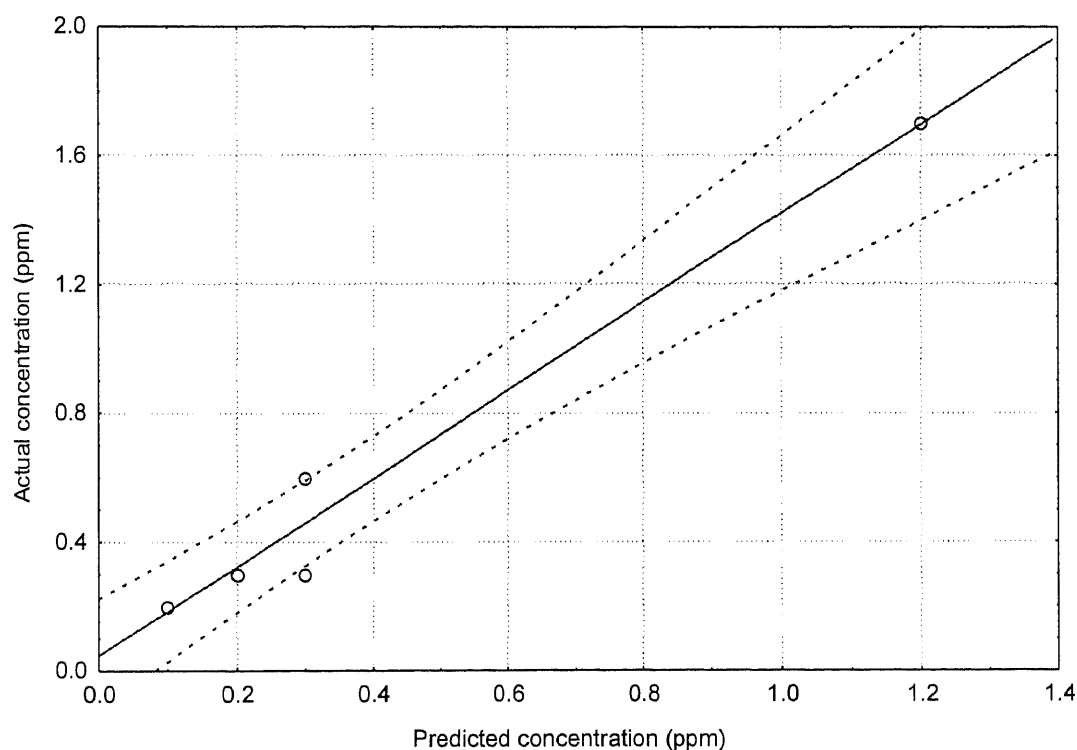


Figure 57 Predicted Concentrations As Compared to Actual Concentration. Sedimentation Water Sample of the RM plant (May 21, 1998). Results Analyzed with 95% Confidence Level. Coefficient of Correlation of 0.98. $y = 1.37(x) + 0.05$ The Limits of the Correlation are 0.1 to 1.2 ppm

The validation continues to hold up well with R of 0.98 being greater than both of the $r_{0.05}$ and $r_{0.01}$

6.3.3 Validation Using Water Samples from the Filtration Units

Data shown below are relevant to the filtration unit at the Passaic Valley WTP (table 24 and figure 58):

Table 24 Summary of Validated Results. Samples from the Filtration Unit of the Passaic Valley Water Treatment Plant. Values are in mg/L (4/28/1998)

Fraction	Concentration (mg/L)	
	Predicted	Observed
HPOB	0.2	0.2
HPOA	0.2	0.3
HPON	0.3	0.4
HPIB	0.2	0.3
HPIA	1.5	1.0
HPIN	0.6	0.2

Weak to moderate correlation exists between the predicted value and the observed as indicated by the above table and figure. The coefficient of correlation tested well against the 5% level of significance but fell short of meeting the 1% criteria level test as calculated earlier in section 6.4.1

With the exception of one data point out of a set of 6 as shown above, the effectiveness of the SFS toolkit is still verified well. The bad data point had weakened the correlation somewhat but the overall validation prevails at R of 0.90 and df is still of 6 less 2 degree of freedom.

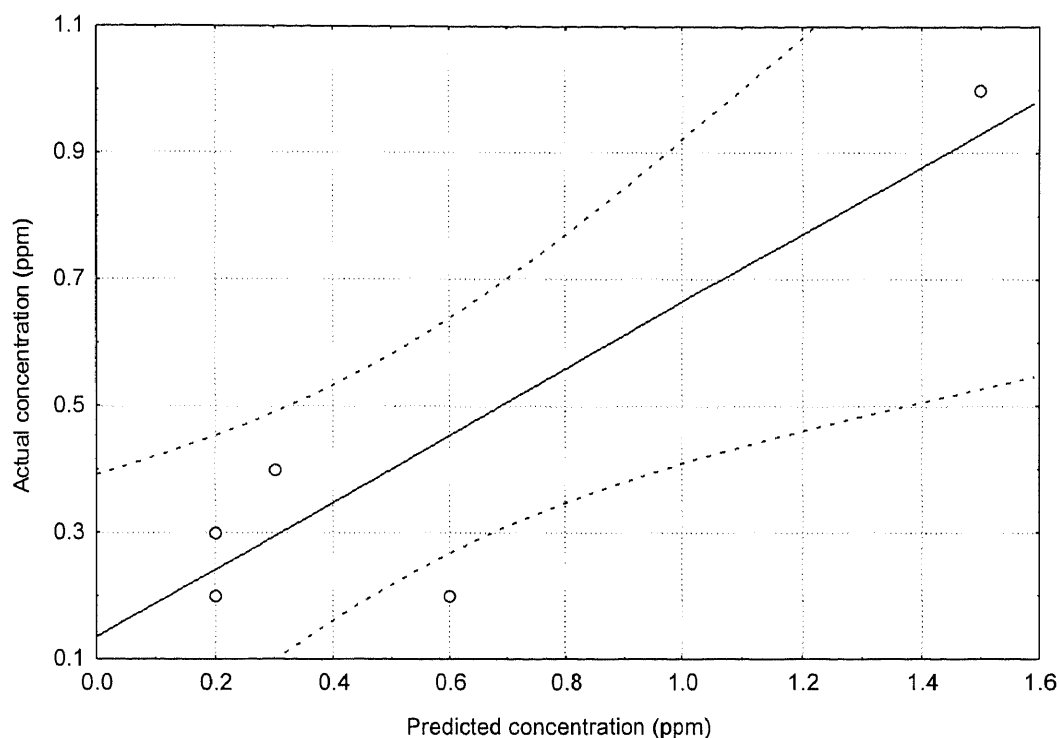


Figure 58 Predicted Concentrations As Compared to Actual Concentration. Filtration Water Sample of the PV Plant (April 28, 1998). Results Analyzed with 95% Confidence Level. Coefficient of Correlation of 0.90. $y = 0.53(x) + 0.14$ The Limits of the Correlation are 0.2 to 1.5 ppm

The validation that follows uses water sample from the filtration unit at the Canal

Road water treatment plant (table 25 and figure 59):

Table 25 Summary of Validated Results. Samples from the Filtration Unit of the Canal Road Water Treatment Plant. Values are in mg/L (5/21/1998)

Fraction	Concentration (mg/L)	
	Predicted	Observed
HPOB	0.02	0.01
HPOA	0.2	0.1
HPON	0.3	0.3
HPIB	0.1	0.1
HPIA	1.1	1.1
HPIN	0.4	0.5

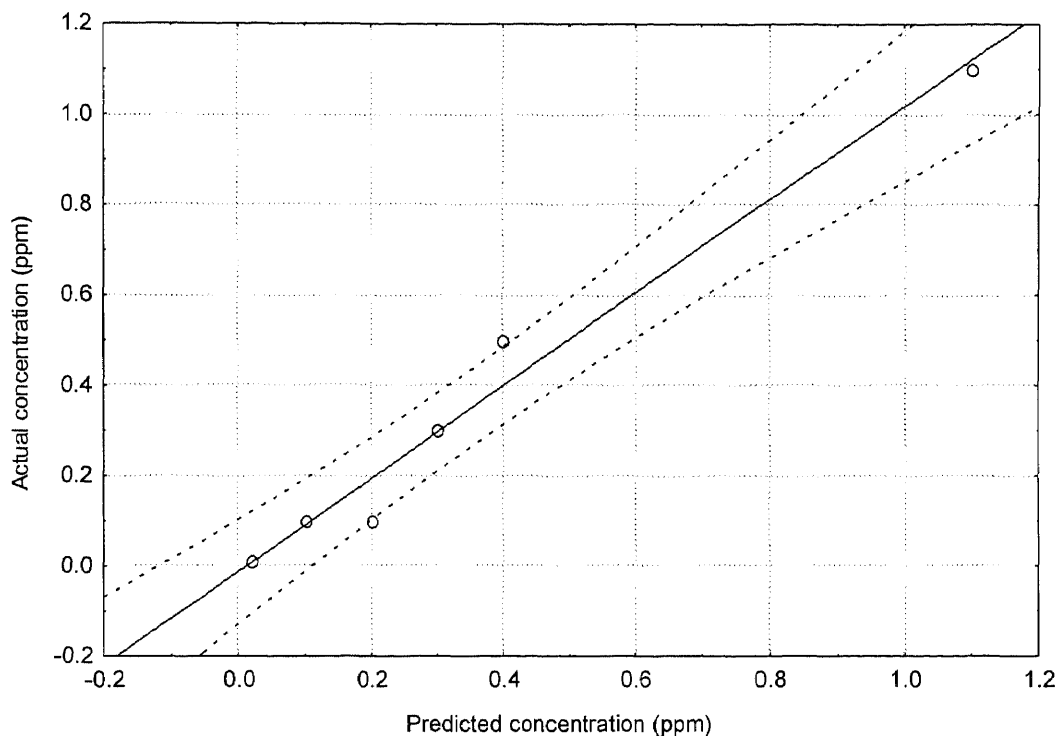


Figure 59 Predicted Concentrations As Compared to Actual Concentration. Filtration Water Sample of the CR plant (May 21, 1998). Results Analyzed with 95% Confidence Level. Coefficient of Correlation of 0.98. $y = 1.03(x) - 0.01$ The Limits of the Correlation are 0.02 to 1.1 ppm

Excellent strength of correlation exists indicative by the coefficient of correlation $R=0.98$ and the significance test at 2 critical values of 5% and 1%.

Water from the filtration unit of the Raritan Millstone conventional treatment plant was used in the following validation of the toolkit (table 26 and figure 60):

Table 26 Summary of Validated Results. Samples from the Filtration Unit of the Raritan Millstone Water Treatment Plant. Values are in mg/L (5/21/1998)

Fraction	Concentration (mg/L)	
	Predicted	Observed
HPOB	0.1	0.1
HPOA	0.1	0.2
HPON	0.3	0.5
HPIB	0.1	0.1
HPIA	1.3	1.4
HPIN	0.2	0.2

Excellent correlation as shown in table 26 above and also in the following figure. This is despite the fact that the toolkit's database is being used outside of its realm.

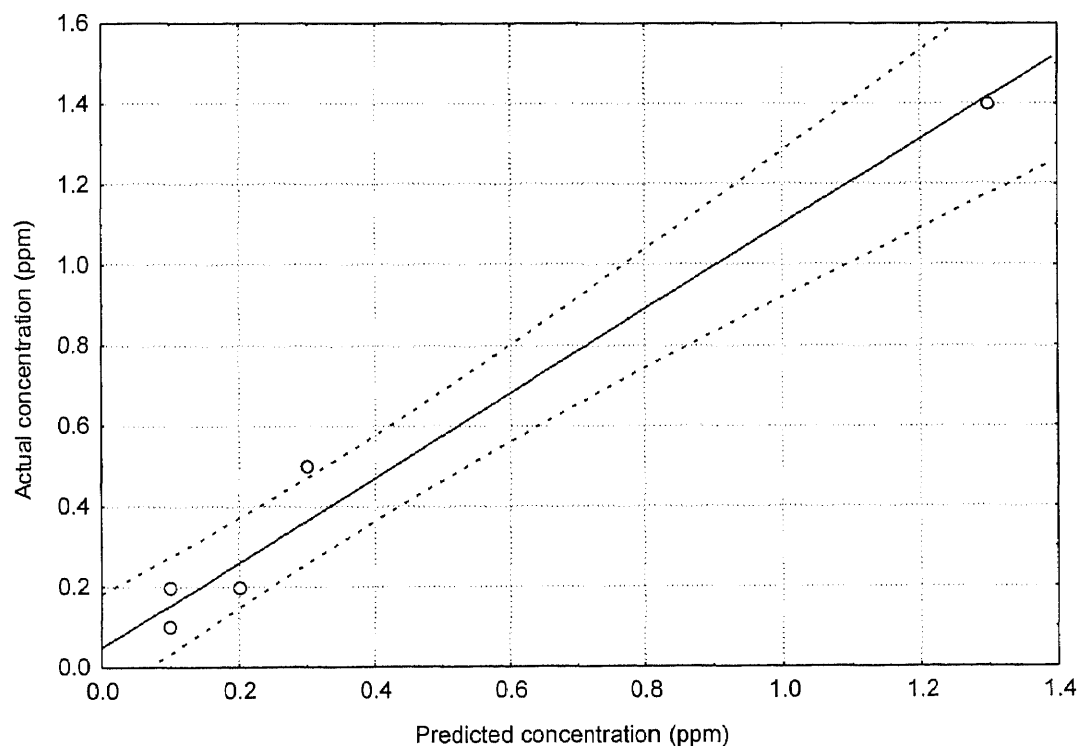


Figure 60 Predicted Concentrations As Compared to Actual Concentration. Filtration Water Sample of the RM Plant (May 21, 1998). Results Analyzed with 95% Confidence Level. Coefficient of Correlation of 0.99. $y = 1.05(x) + 0.05$ The Limits of the Correlation are 0.1 to 1.3 ppm

6.3.4 Validation Using Water Samples from the Effluent of the WTP

Water sample from the Passaic Valley WTP's effluent were used in the following validation and discussion (table 27 and figure 61):

Table 27 Summary of Validated Results. Samples from the Effluent of the Passaic Valley Water Treatment Plant. Values are in mg/L (4/28/1998)

Fraction	Concentration (mg/L)	
	Predicted	Observed
HPOB	0.2	0.2
HPOA	0.2	0.2
HPON	0.3	0.3
HPIB	1.3	0.8
HPIA	0.2	0.2
HPIN	1.0	0.2

In this case of the validation of results using the effluent water of the PV plant, the verification fails the test through the use of the 2 levels of significance at 1% and 5% as discussed before. Realizing data the bad data point of the HPIN, the coefficient of correlation tests well against the above-mentioned level of significance when this point was excluded. The result is shown below in figure 61:

$R = 0.99$ is greater than both $r_{0.05}$ (0.88) and $r_{0.01}$ (0.96).

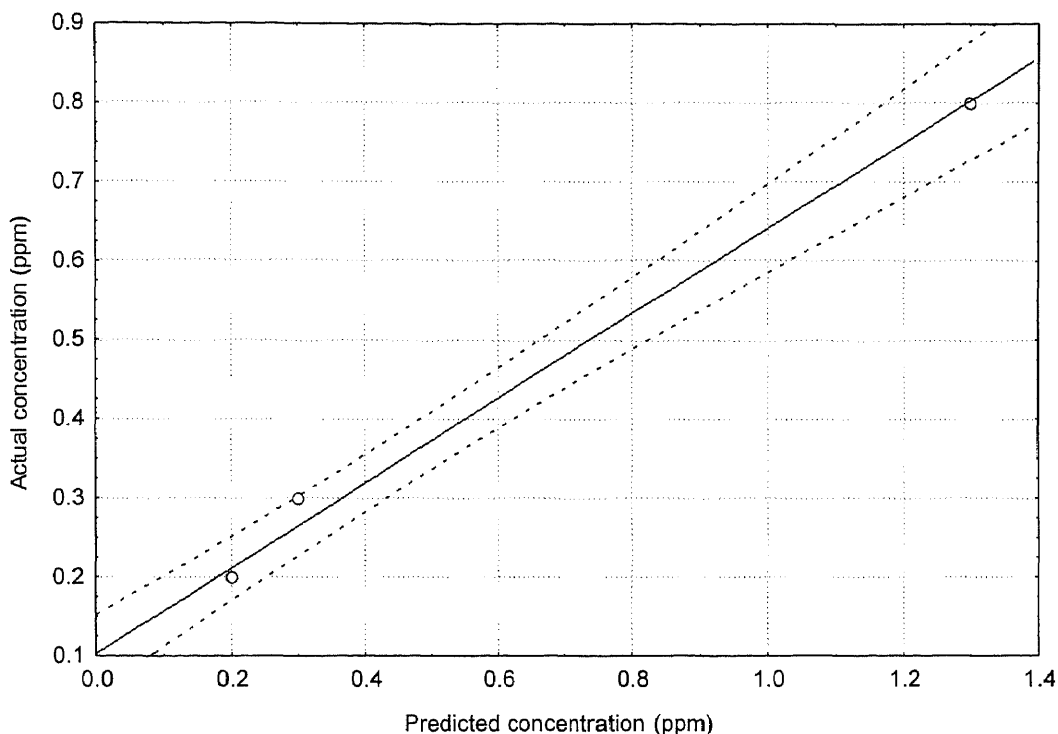


Figure 61 Predicted Concentrations As Compared to Actual Concentration. Effluent Water Sample of the PV Plant (April 28, 1998). Results Analyzed with 95% Confidence Level. Coefficient of Correlation of 0.99. $y = 0.54(x) + 0.10$ The Limits of the Correlation are 0.2 to 1.3 ppm

The following validation uses water sample from the Canal Road WTP's effluent (table 28 and figure 62):

Table 28 Summary of Validated Results. Samples from the Effluent of the Canal Road Water Treatment Plant. Values are in mg/L (5/21/1998)

Fraction	Concentration (mg/L)	
	Predicted	Observed
HPOB	0.03	0.01
HPOA	0.2	0.1
HPON	0.3	0.3
HPIB	0.1	0.1
HPIA	1.1	0.9
HPIN	0.1	0.5

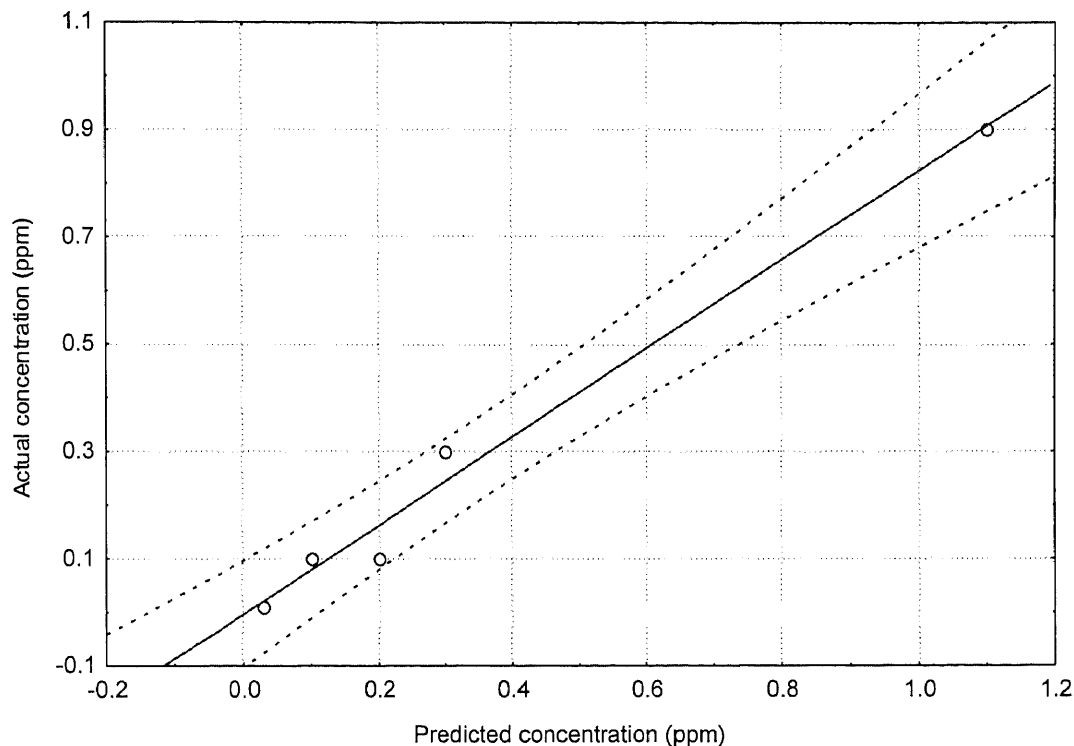


Figure 62 Predicted Concentrations As Compared to Actual Concentration. Effluent Water Sample of the CR Plant (May 21, 1998). Results Analyzed with 95% Confidence Level. Coefficient of Correlation of 0.99. $y = 0.83(x) - 0.004$ The Limits of the Correlation are 0.03 to 1.1 ppm

Good correlation exists given a 95% band of confidence as shown above and a coefficient of correlation of 0.99, which is consistently tested well against the 2 levels of significance criteria using df of 5 less 2 degrees of freedom (Martin Sternstein, 1994).

Water from the effluent of the Raritan Millstone WTP shows the following validation of the SFS toolkit (table 29 and figure 63):

Table 29 Summary of Validated Results. Samples from the Effluent of the Raritan Millstone Water Treatment Plant. Values are in mg/L (5/21/1998)

Fraction	Concentration (mg/L)	
	Predicted	Observed
HPOB	0.1	0.1
HPOA	0.1	0.2
HPON	0.3	0.5
HPIB	0.1	0.2
HPIA	1.3	1.1
HPIN	0.2	0.2

Indicative by the statistics on the following figure, the SFS toolkit continues to be validated very well.

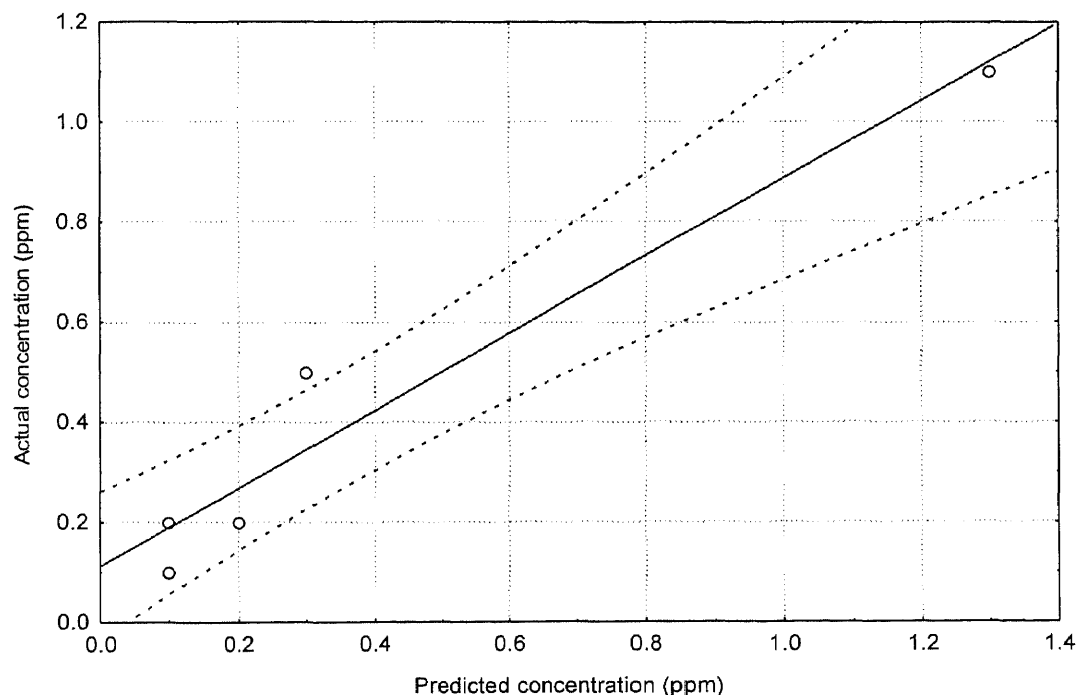
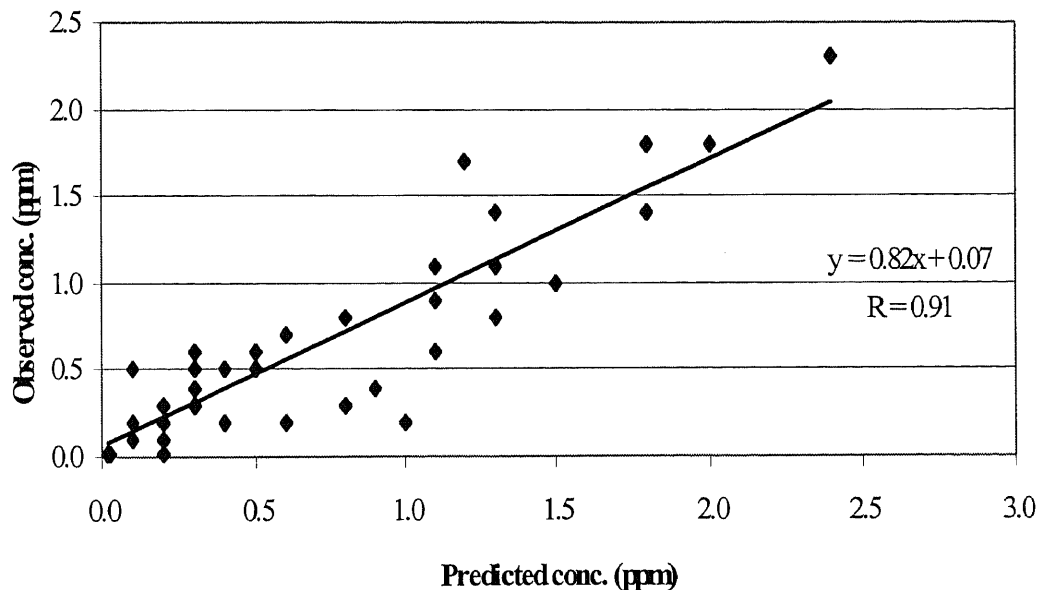


Figure 63 Predicted Concentrations As Compared to Actual Concentration. Effluent Water Sample of the RM Plant (May 21, 1998). Results Analyzed with 95% Confidence Level. Coefficient of Correlation of 0.97. $y = 0.80(x) + 0.11$ The Limits of the Correlation are 0.1 to 1.3 ppm

Moving from validating at each treatment station one at a time, the following shows the validation of the SFS methodology using composite data from all 12 treatment unit operation of all three plants. Predicted values were well correlated observed parameters as shown in the following figure 64. Strength of the correlation was against confirmed through the two critical r values of 5% and 1%. As an alternate check, paired t -ratio of 1.71 was checked against the t critical value of 2.00 for a df of 69 and α value of 0.025 at each tail end.



Not only SFS yields good prediction of precursor concentration as shown above, precursor concentration correlates well with the formation potential of THM. As shown in the following figure, the coefficient of correlation of $R = 0.94$ compares well with the $r_{0.01}$ and $r_{0.05}$ values of the two level of significance test criteria using 7 sample points. These two values are 0.874 and 0.754, respectively (Martin Sternstein, 1994).

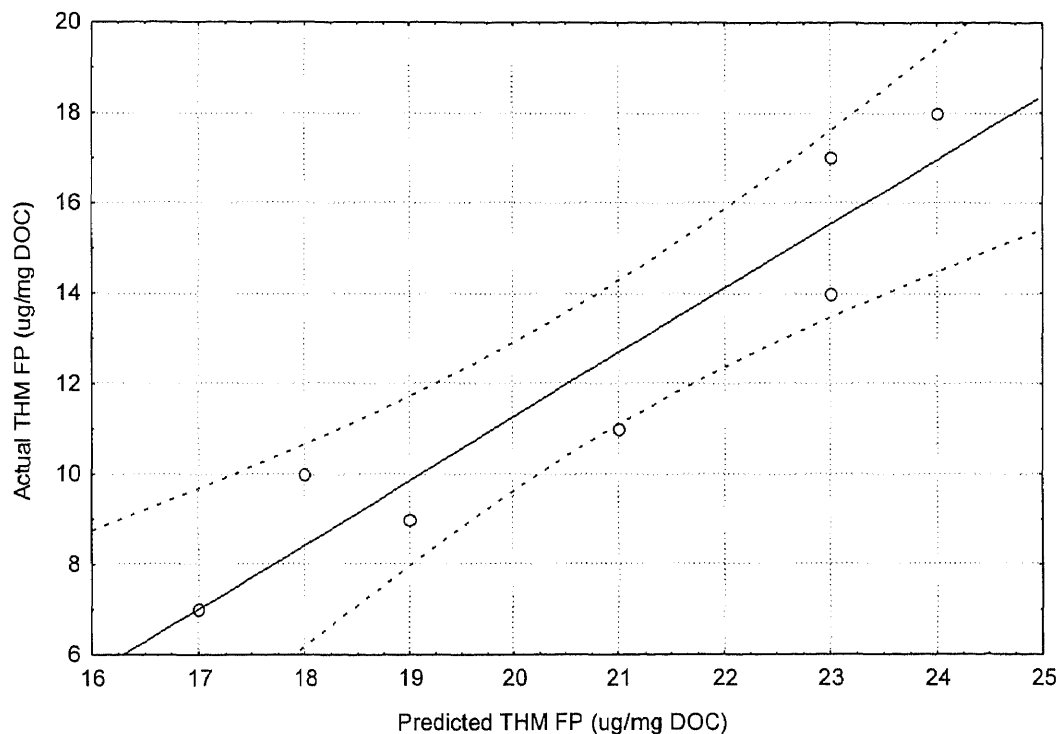


Figure 65 Verification of THM FP (predicted vs. actual value) at 95% Confidence Level with Coefficient of Correlation of 0.94; $y = 1.42(x) - 17.2$ Verification Was Conducted at the Following 7 sample Points: Basin and Effluent of the CR plant, Effluent of the RM plant and the entire treatment train of the PV Plant.

With regard to the validation for the HAA FP, the following result shows good correlation exists with R of 0.94 as confirmed again by the 1% and 5% criteria of the 2-level of significance test.

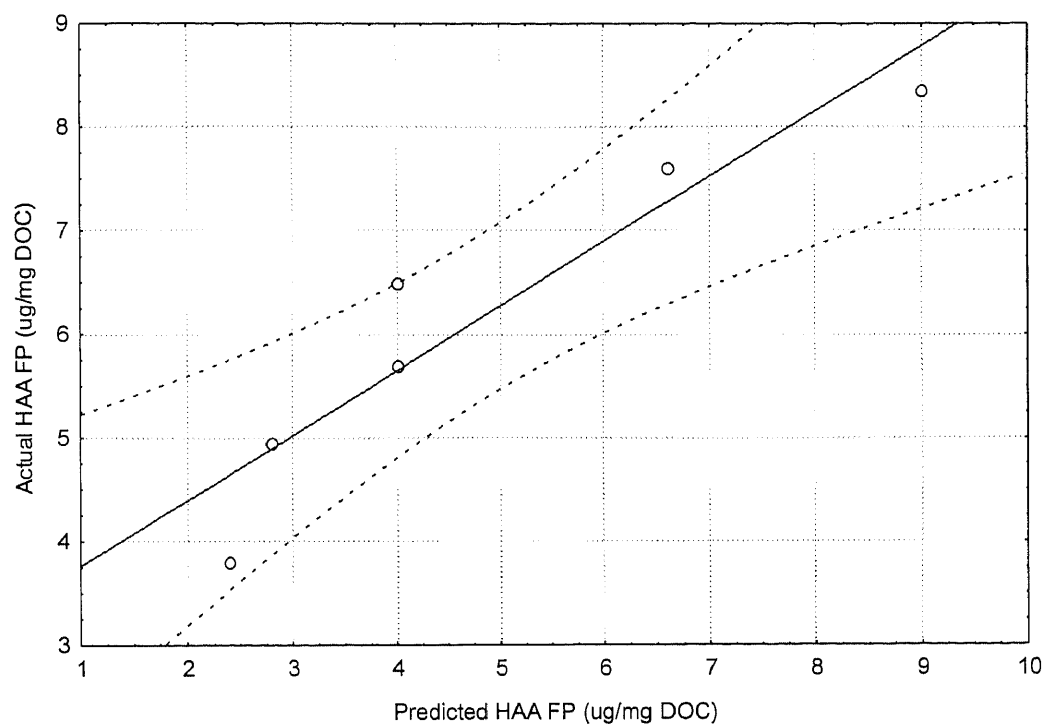


Figure 66 Verification of HAA FP (predicted vs. actual value) at 95% Confidence Level with Coefficient of Correlation of 0.94; $y = 0.63(x) + 3.14$ Verification Was Conducted at the Following 6 Sample Points: Influent, Filtration and Effluent of the CR plant, Filtration and Effluent of the RM plant and the Effluent of the PV plant.

6.4 Proposed Application of Precursor Removal Optimization Method

Because of the shortfalls of the current analytical methods, which are (1) taking too long to produce the information required of a dynamic pollution control problem, and (2) not knowing the specific DBP precursors to focus and prioritize the resources for the problem solving, this research proposes an alternative. While the alternative is not an on-line method, it is much faster and more efficient than the current approaches. Faster because it uses a spectral fluorescent signature (SFS) scanning tool. More efficient because it identifies which precursor has the most formation potential of DBPs that ought to be removed first.

There are basically three steps in the optimization of the DBP precursor removal. This research accomplishes the first two, which are (1) rapidly identify the DBP precursors by SFS scanning and analysis, and (2) promptly quantify the problematic precursor in terms of its DBP formation potential. The third step is to engineer an operation unit that is able to remove the targeted precursor(s). This is outside the scope of this research and remains to be an area of recommendation for further study.

To rapidly identify and quantify the targeted precursor, the following procedure is proposed:

6.4.1 Sample Preparation

1. Take a 500-ml sample from the water intake. Verify or adjust the pH to 7 and its temperature to room setting of about 25 C.
2. Filter the sample with a 0.45-um paper.

6.4.2 Fluorescent Spectrophotometer Preparation and Operation

3. Verify calibration or calibrate the Spectrometer as specified by the manufacturer.
4. Install a scanning program to instruct the spectrophotometer to scan the water sample using a 12-nm backward step starting with excitation of 525-nm wavelength to 225-nm wavelength. For each excitation wavelength, record the fluorescent spectra from (excitation wavelength +24 nm) to 633 nm. This is called the raw SFS data file of the water sample. Copy the SFS raw data file onto a floppy disk.

6.4.3 Using the SFS Toolkit

5. Load a compatible Visual Basic (VB) program (v. 5 or later) from a desktop.
6. Install the SFS toolkit program onto the VB software directory in the computer. This program is listed in its entirety in appendix B1 for reference.
7. Open the SFS toolkit file from VB and RUN the program
8. Enter UserID and Password to go beyond the signon screen
9. On the next screen (SFS Toolkit form), prompt the computer to read the raw data file
10. Respond as to where the raw data file is located. If raw data is to be stored in the C drive, make and store data file into the SFS toolkit directory in the C drive of the desktop. Otherwise, floppy A drive can be used.
11. After receiving confirmation that data has been read and loaded successfully, follow the prompt provided by the screen by
 - Selecting the fraction to be COMPUTED for its concentration.

- Once concentration has been calculated, ensure to RECORD the result on the specified screen and GO BACK to select another fraction to work on until all six fractions have been selected and computed.

12. Proceed to calculate the formation potential of THM or HAA or HAN

13. The expected results are

- List of precursors in the water sample ranked by the concentration
- Treatment priority listed by formation potential

6.4.4 Proposed Application of SFS Toolkit

The following discussion is focused on trihalomethanes as the disinfection by-product. The discussion, however, is equally well applicable to haloacetic acids and haloacetonitriles whose results were presented elsewhere in this publication.

It is widely recognized that measurements of the concentrations of disinfection by-products and their precursors are labor intensive and time-consuming (McClellan *et al.*, 1996). For this reason, correlation, models and analytical techniques (McClellan *et al.*, 1996; Hofman and Andrews, 1996) have been proposed to speed up the process to rise to the challenge presented by disinfection by-products problem that is in itself truly dynamic in nature.

Since Spectral Fluorescent Signature (SFS) has been shown to be a useful analytical tool to identify and quantify DOM (Orlov *et al.*, 1995; Chubarov *et al.*, 1994; Babichenko *et al.*, 1995) and the different DBP precursors, the following example is illustrated using the SFS toolkit:

A water sample is picked up from an intake bay of a water treatment plant having TOC of 4 mg/L and a nominal flow rate of 55 MGD.

Questions:

- (1) What is the trihalomethane formation potential of the water sample?
- (2) Which fractions must be removed to best meet the regulations on TTHMs?

The water sample is to run through a 0.45-micron filter after which it is subject to a scan by a fluorescent spectrophotometer. The data is then fed into the SFS Toolkit to search, match and output the entire list of DBP precursors in terms of precursor type and precursor concentration in ppm as following:

- Hydrophobic base 0.1 ppm
- Hydrophobic acid 0.4 ppm
- Hydrophobic neutral 0.5 ppm
- Hydrophilic base 0.1 ppm
- Hydrophilic acid 1.8 ppm
- Hydrophilic neutral 0.8 ppm

Having identified and quantified the DOM precursors as shown above, each DBP precursor will then be used as input to the correlation database to calculate the formation potentials of the individual type of disinfection by-products. The following are the results:

• Hydrophobic base	4 ppb	thm fp
• Hydrophobic acid	6 ppb	thm fp
• Hydrophobic neutral	13 ppb	thm fp
• Hydrophilic base	6 ppb	thm fp
• Hydrophilic acid	39 ppb	thm fp
• Hydrophilic neutral	16 ppb	thm fp

Answer 1: Total THM formation potential of the water sample is 84 ppb of which 46% is from the hydrophilic acid fraction.

Answer 2: Remove the hydrophilic acid fraction first will place the plant about 56 % under the regulated level.

6.4.5 Other Proposed Applications of the SFS Toolkit

- Timely decision can be made to switch to a different source water when high level of targeted precursor is detected. At present, this decision is made based on TOC level, which could be misleading and wasteful of efforts and resources.
- Quick results can be used to vary the dosage of coagulation either to enhance it for better settling or reduce it to eliminate waste.
- Quick results can enhance the development of polymers that may be suitable for the removal of certain problematic fractions.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

. The following conclusions are based on the source water and methods described herein:

1. The modified fractionation procedure that was employed in this research was effective for the isolation and extraction of DOM.
2. Fractionation gave important information about the role that each finite fraction plays in the performance of the different unit operations and in the formation potential of each class of DBPs.
3. Hydrophilic acid was the most abundant fraction in terms of the overall mass of DOM.
4. The removal of fraction mass differs from one disinfection method to the other. For the same source water, the ozonation plant removed more overall precursors than the chlorination plant.
5. With respect to each DOM fraction, the formation potentials of THMs and HAAs were reduced along the treatment train in the water treatment plants. Coagulation and sedimentation were still the locations along the treatment trains to experience the most of the reduction in DBP FP.
6. The variation of DBP FP is influenced by the type of disinfection process (ozonation vs. chlorination) as well as the source waters.

The SFS method

7. Correlated the six fractions' fluorescent characteristics with their corresponding concentrations.
8. Provided spectral identification criteria of different fractions through the peak spectrum's shape factor (SF) which is the product of the peak spectrum's area under the curve (A_p) and the rising slope of the spectrum's peak
9. Identified the most problematic precursor to different class of DBP FP: the hydrophilic acid was most responsible for the formation of THMs. The hydrophobic neutral was the counterpart with respect to HAAs. Conventional unit operations were not effective in removing these fractions. Regardless whether the fractions can be removed easily or not, the need for a rapid method is required to identify the problematic fractions. This is key for on-line application and for studies toward the optimization of the removal of such fractions.
10. Provided validation that SFS database can be established to contain the spectral signature of each fraction at different concentration level. Searching this database using the characteristic SF yielded very good prediction of the measured DOM fraction's concentration. Correlation of coefficient was greater than 0.90
11. Showed that the SFS technique has the potential of being valuable in water treatment, source water assessment and protection.
12. Proved SFS technique as a screening tool, which can provide rapid identification of the precursors. This can be accomplished by use of the SFS graphical user interface, namely, the SFS Toolkit computer program.

13. Demonstrated that selective removal of DBP precursors can be implemented to the extent that less chemical is used to avoid unnecessary exposure of human to chemical's byproducts and side effects, and finally
14. Showed that SFS can be used as sixty-minute solution to the environmental problem of studying the DBP FP. This is a milestone in analytical time reduction!

7.2 Recommendations

Because the tools and techniques presented by this research is the first generation of this finite fraction method of DBP analysis, further research in the following areas are recommended:

1. Refine the technique that this research has established
 - Explore other identifiable signatures that are unique to the fluorescent spectra
 - Increase the database by fractionating more samples at broader range and narrower increments of the DOC. The database should be catalogued in terms of locations and in terms of the varying times of the year.
2. Shorten the fluorescent scanning time to make it possible for on-line application of the method. Once this is accomplished, it is anticipated that watershed monitoring for DBP control can be added to the plant's supervisory and control automated data acquisition (SCADA) system.
3. Contemplate other fractionation methods. Among the fractionation methods being recommended are (a) membrane fractionation and (b) flow field fractionation (FFF).
4. Engineer and design a treatment method to remove the problematic precursors that have been identified by this research.

5. Improve upon the limitations of the technique at the present time:

- Formation potential test the fractions at conditions other than the standard ones of 7 pH, 25 degree C temperature and 100 mg/L chlorine dosage.
- Fractionate samples at varying water quality conditions throughout the year to learn the seasonal effect on the technique.
- Verify the applicability of the technique at other locations (than the intake) and at other source waters (than the Passaic and Raritan-Millstone Rivers).

APPENDIX A

FIGURES

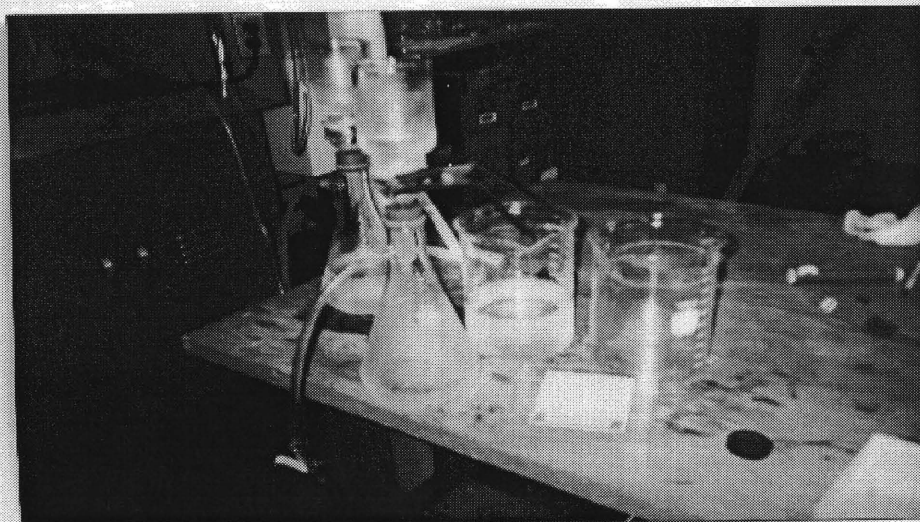


Figure A1 Vacuum Filtration Setup to Transform Water Samples from TOC to DOC using 0.45-um Filter Whatman Paper

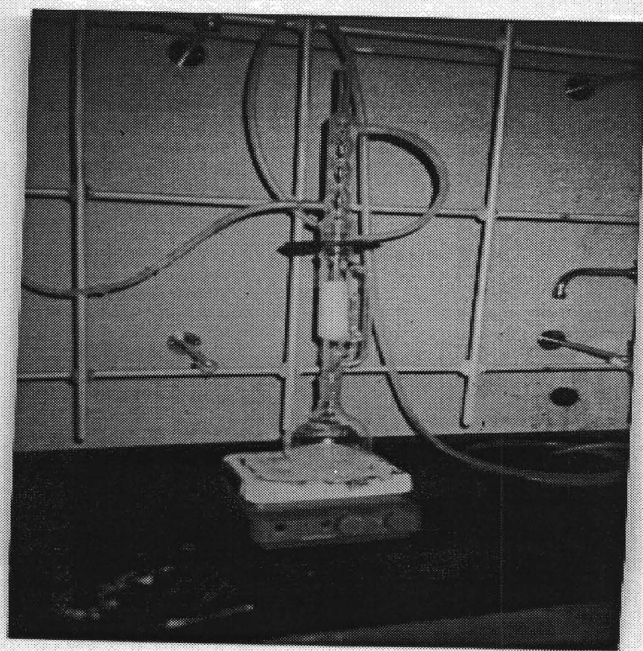


Figure A2 A Typical Soxhlet Extraction Setup for the Purification of DAX-8, AG-MP-0 and Duolite A7 Resin in Preparation for the DOM Fractionation Procedure

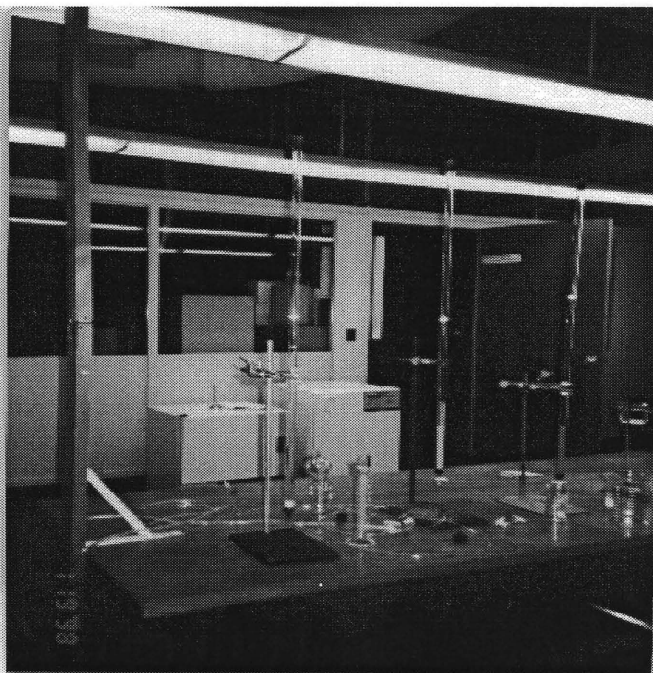


Figure A3 A 3-Chromatographic Resin Adsorption Column Fractionation Setup. From left to right are DAX-8 Column for the Isolation of Hydrophobic Base, Acid and Neutral; AG-MP-50 Column for the Isolation of Hydrophilic Base; and Duolite A7 Column for the Isolation of Hydrophilic Acid and Neutral.

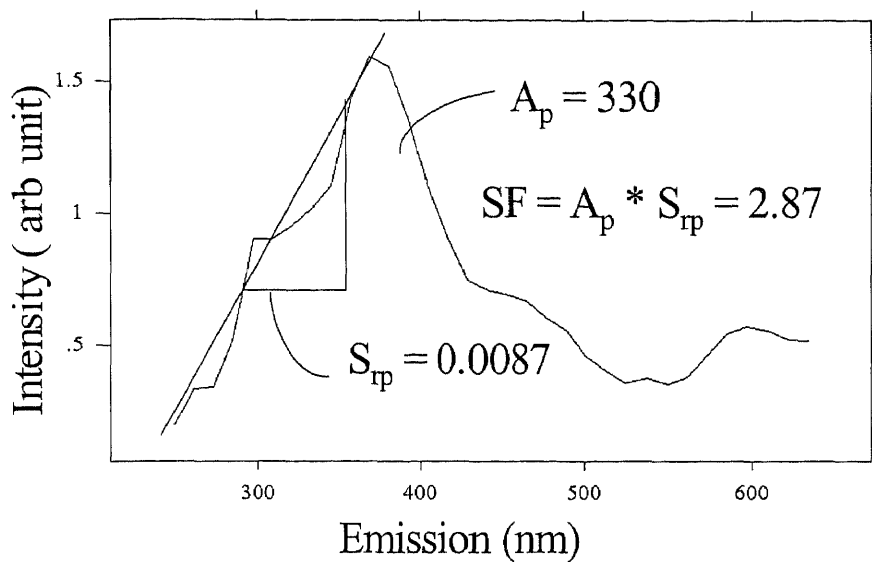


Figure A4 Major Peak Spectrum of the Hydrophobic Base Fraction at 0.1 ppm

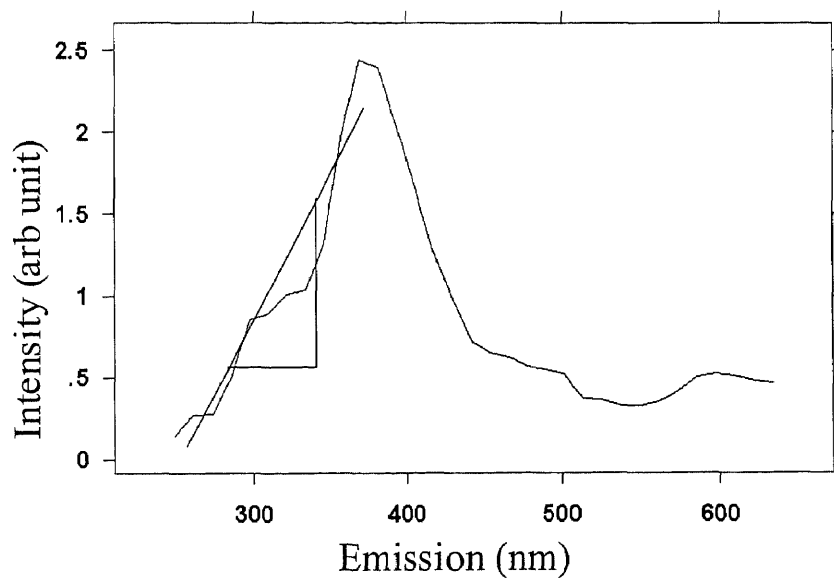


Figure A5 Major Peak Spectrum of the Hydrophobic Base Fraction at 0.2 ppm

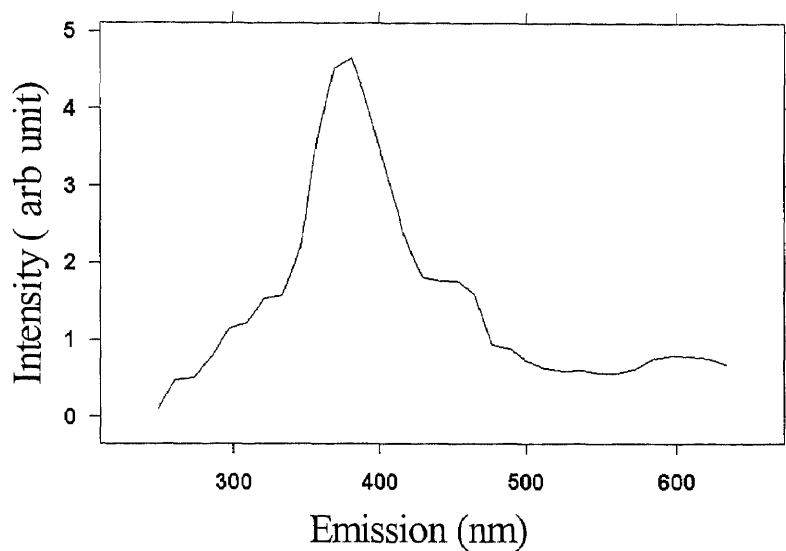


Figure A6 Major Peak Spectrum of the Hydrophobic Base Fraction at 0.4 ppm

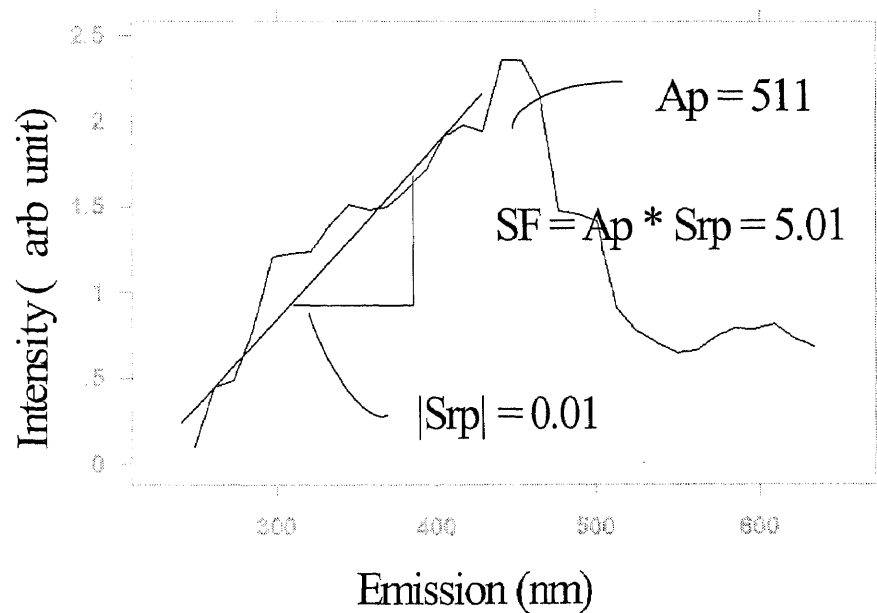


Figure A7 Major Peak Spectrum of the Hydrophobic Acid Fraction at 0.4 ppm

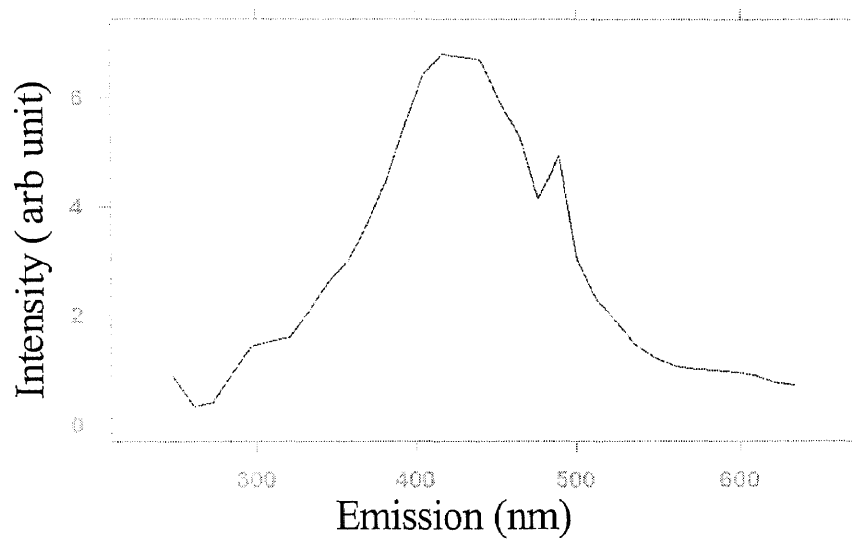


Figure A8 Major Peak Spectrum of the Hydrophobic Acid Fraction at 2 ppm

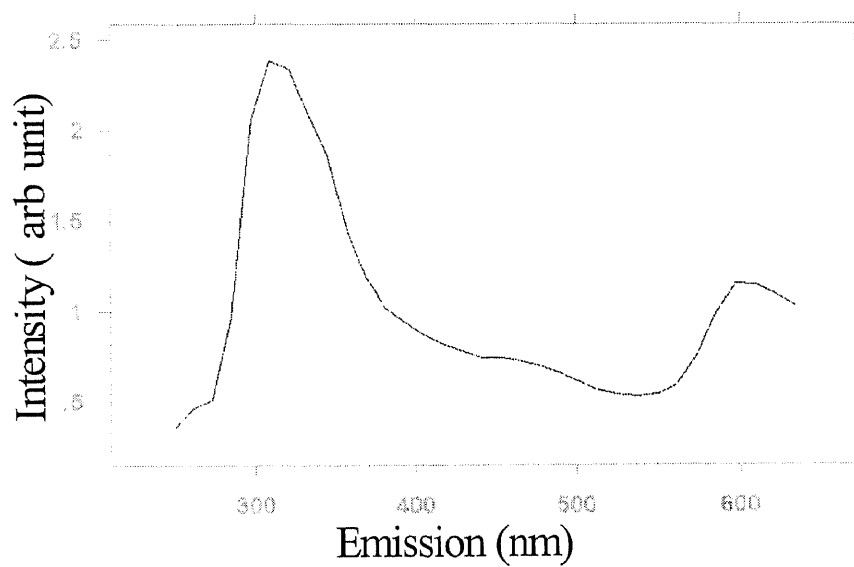


Figure A9 Major Peak Spectrum of the Hydrophobic Neutral Fraction at 0.1 ppm

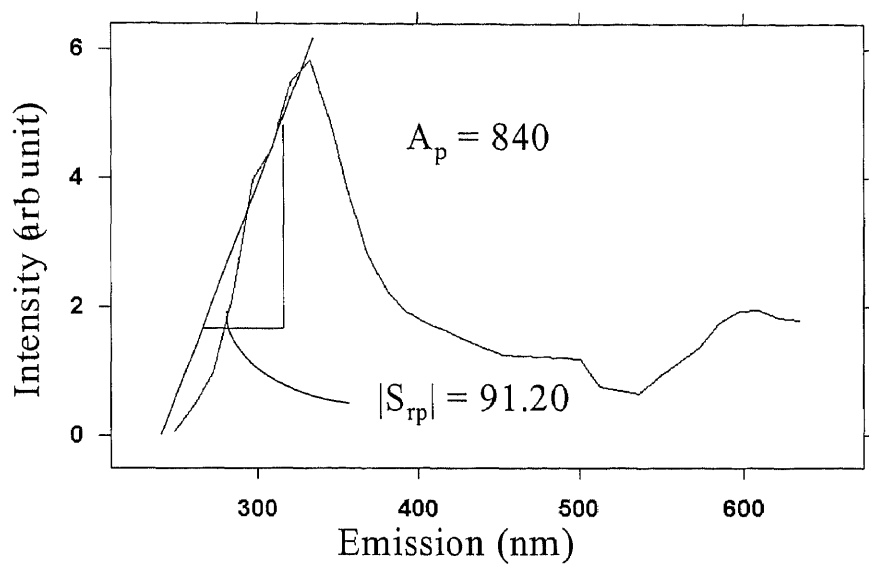


Figure A10 Major Peak Spectrum of the Hydrophobic Neutral Fraction at 0.6 ppm

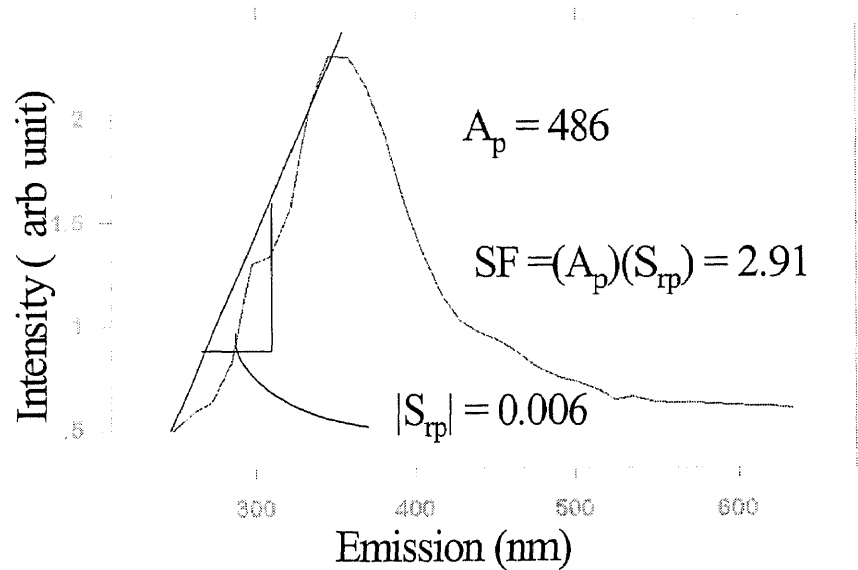


Figure A11 Major Peak Spectrum of the Hydrophilic Base Fraction at 0.1 ppm

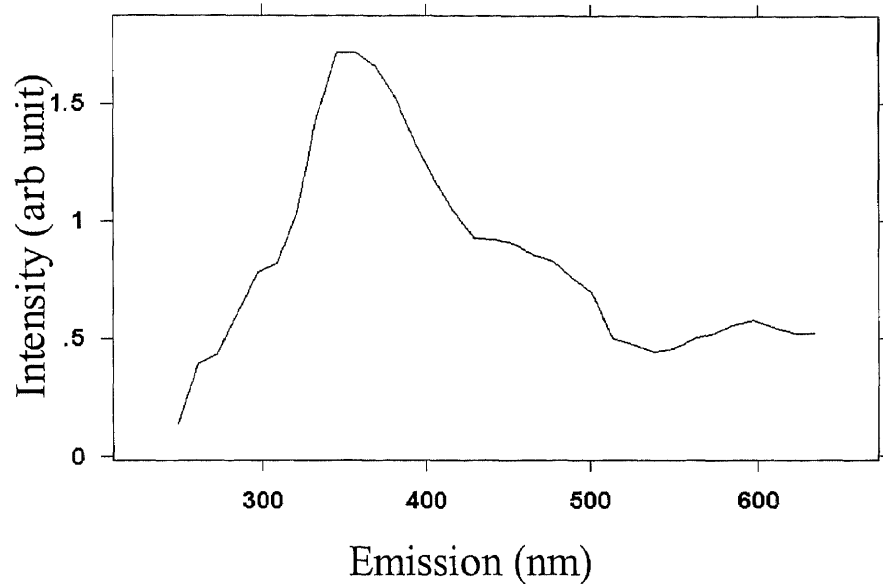


Figure A12 Major Peak Spectrum of the Hydrophilic Base Fraction at 0.4 ppm

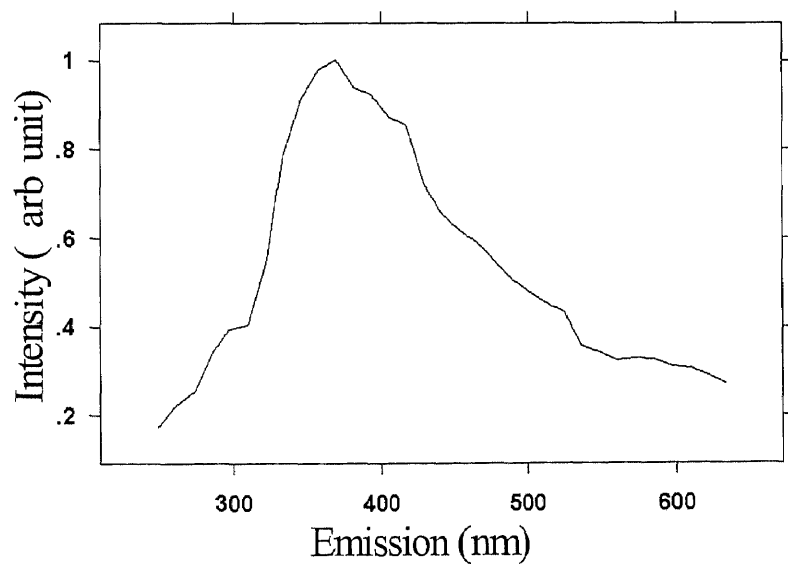


Figure A13 Major Peak Spectrum of the Hydrophilic Acid Fraction at 1 ppm

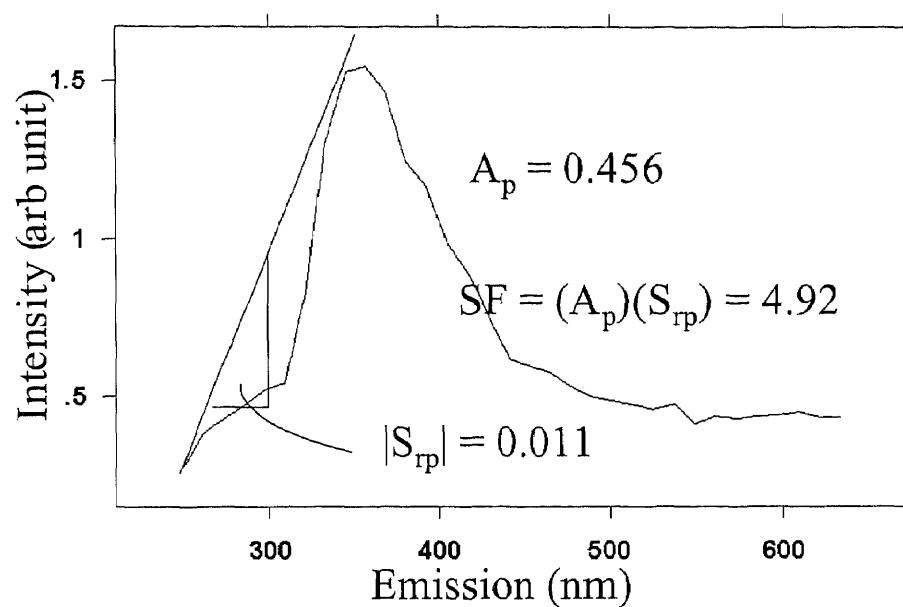


Figure A14 Major Peak Spectrum of the Hydrophilic Acid Fraction at 2 ppm

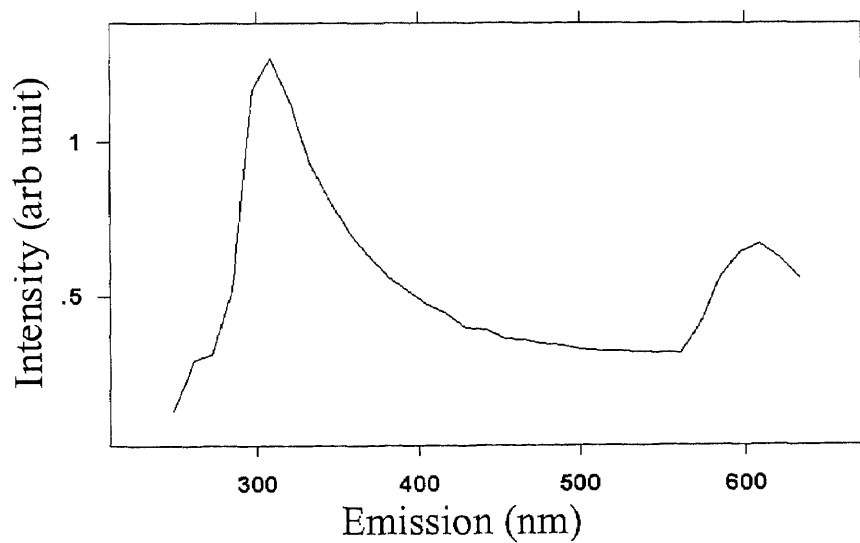


Figure A15 Major Peak Spectrum of the Hydrophilic Neutral Fraction at 0.6 ppm

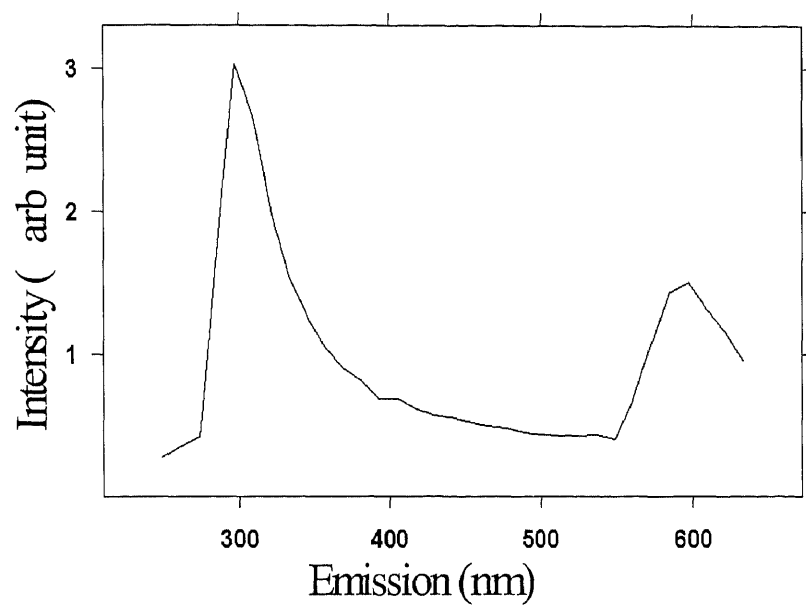


Figure A16 Major Peak Spectrum of the Hydrophilic Neutral Fraction at 0.8 ppm

APPENDIX B

COMPUTER CODE FOR DBP PRECURSOR PREDICTIVE MODEL

```
Private Sub cmdCancel_Click()

frmWelcome.Hide

frmYourInput.Hide

frmYourResponse.Hide

frmToolkit.Hide

frmReadData.Hide

frmFractionIDHPOB.Hide

frmFractionIDHPOA.Hide

frmFractionIDHPON.Hide

frmFractionIDHPIB.Hide

frmFractionIDHPIA.Hide

frmFractionIDHPIN.Hide

frmErrorMessage.Hide

MsgBox "Good Bye"

End Sub

Private Sub cmdOK_Click()

If txtPassword.Text = "" Then

frmToolkit.Show

Else

MsgBox "Sorry, You Are Not Authorized to Use This Program"

End If
```

Missing Page

End Sub

Private Sub cmdContDBPComp_Click()

frmYourInput.Show

End Sub

Private Sub cmdExit_Click()

frmToolkit.Hide

frmWelcome.Show

End Sub

Private Sub cmdReadfile_Click()

frmReadData.Show

End Sub

Private Sub cmdRecord_Click()

frmYourInput.Show

End Sub

Private Sub cmdRestart_Click()

frmWelcome.Show

End Sub

Private Sub cmdslopeHPIA_Click()

picResult.Cls

Dim ex_225(1 To 33, 1 To 2) As Single

Dim ex_237(1 To 32, 1 To 2) As Single

Dim ex_249(1 To 31, 1 To 2) As Single

Dim ex_261(1 To 30, 1 To 2) As Single

Dim ex_273(1 To 29, 1 To 2) As Single

Dim ex_285(1 To 28, 1 To 2) As Single

Dim ex_297(1 To 27, 1 To 2) As Single

Dim ex_309(1 To 26, 1 To 2) As Single

Dim ex_321(1 To 25, 1 To 2) As Single

Dim ex_333(1 To 24, 1 To 2) As Single

Dim ex_345(1 To 23, 1 To 2) As Single

Dim ex_357(1 To 22, 1 To 2) As Single

Dim ex_369(1 To 21, 1 To 2) As Single

Dim ex_381(1 To 20, 1 To 2) As Single

Dim ex_393(1 To 19, 1 To 2) As Single

Dim ex_405(1 To 18, 1 To 2) As Single

Dim ex_417(1 To 17, 1 To 2) As Single

Dim ex_429(1 To 16, 1 To 2) As Single

Dim ex_441(1 To 15, 1 To 2) As Single

Dim ex_453(1 To 14, 1 To 2) As Single

Dim ex_465(1 To 13, 1 To 2) As Single

Dim ex_477(1 To 12, 1 To 2) As Single

Dim ex_489(1 To 11, 1 To 2) As Single

Dim ex_501(1 To 10, 1 To 2) As Single

Dim ex_513(1 To 9, 1 To 2) As Single

Dim ex_525(1 To 8, 1 To 2) As Single

Dim em_225(1 To 33), em_237(1 To 32), em_249(1 To 31),

em_261(1 To 30), _
 em_273(1 To 29), em_285(1 To 28), em_297(1 To 27),
 em_309(1 To 26), _
 em_321(1 To 25), em_333(1 To 24), em_345(1 To 23),
 em_357(1 To 22), _
 em_369(1 To 21), em_381(1 To 20), em_393(1 To 19),
 em_405(1 To 18), _
 em_417(1 To 17), em_429(1 To 16), em_441(1 To 15),
 em_453(1 To 14), _
 em_465(1 To 13), em_477(1 To 12), em_489(1 To 11),
 em_501(1 To 10), _
 em_513(1 To 9), em_525(1 To 8) As Integer
 Dim Value_225(1 To 33), Value_237(1 To 32), Value_249(1 To
 31),
 Value_261(1 To 30), _
 Value_273(1 To 29), Value_285(1 To 28), Value_297(1 To 27),
 Value_309(1 To 26), _
 Value_321(1 To 25), Value_333(1 To 24), Value_345(1 To 23),
 Value_357(1 To 22), _
 Value_369(1 To 21), Value_381(1 To 20), Value_393(1 To 19),
 Value_405(1 To 18), _
 Value_417(1 To 17), Value_429(1 To 16), Value_441(1 To 15),
 Value_453(1 To 14), _

Value_465(1 To 13), Value_477(1 To 12), Value_489(1 To 11),
 Value_501(1 To 10), _
 Value_513(1 To 9), Value_525(1 To 8), slopeHPOB As Single
 Dim size225, size237, size249, size261, size273, size285,
 size297, _
 size309, size321, size333, size345, size357, size369, size381, _
 size393, size405, size417, size429, size441, size453, size465, _
 size477, size489, size501, size513, size525 As Integer

 size225 = 33

 size237 = 32

 size249 = 31

 size261 = 30

 size273 = 29

 size285 = 28

 size297 = 27

 size309 = 26

 size321 = 25

 size333 = 24

 size345 = 23

 size357 = 22

 size369 = 21

 size381 = 20

 size393 = 19

size405 = 18

size417 = 17

size429 = 16

size441 = 15

size453 = 14

size465 = 13

size477 = 12

size489 = 11

size501 = 10

size513 = 9

size525 = 8

Open "c:\SFStoolkit\ex_225.prn" For Input As #1

For i = 1 To 33

Input #1, em_225(i), Value_225(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_237.prn" For Input As #1

For i = 1 To 32

Input #1, em_237(i), Value_237(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_249.prn" For Input As #1


```
For i = 1 To 31

    Input #1, em_249(i), Value_249(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_261.prn" For Input As #1

    For i = 1 To 30

        Input #1, em_261(i), Value_261(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_273.prn" For Input As #1

    For i = 1 To 29

        Input #1, em_273(i), Value_273(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_285.prn" For Input As #1

    For i = 1 To 28

        Input #1, em_285(i), Value_285(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_297.prn" For Input As #1

    For i = 1 To 27

        Input #1, em_297(i), Value_297(i)

    Next i
```

Close #1

Open "c:\SFStoolkit\ex_309.prn" For Input As #1

For i = 1 To 26

Input #1, em_309(i), Value_309(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_321.prn" For Input As #1

For i = 1 To 25

Input #1, em_321(i), Value_321(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_333.prn" For Input As #1

For i = 1 To 24

Input #1, em_333(i), Value_333(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_345.prn" For Input As #1

For i = 1 To 23

Input #1, em_345(i), Value_345(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_357.prn" For Input As #1

```
For i = 1 To 22

    Input #1, em_357(i), Value_357(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_369.prn" For Input As #1

    For i = 1 To 21

        Input #1, em_369(i), Value_369(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_381.prn" For Input As #1

    For i = 1 To 20

        Input #1, em_381(i), Value_381(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_393.prn" For Input As #1

    For i = 1 To 19

        Input #1, em_393(i), Value_393(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_405.prn" For Input As #1

    For i = 1 To 18

        Input #1, em_405(i), Value_405(i)

    Next i
```

Close #1

Open "c:\SFStoolkit\ex_417.prn" For Input As #1

For i = 1 To 17

Input #1, em_417(i), Value_417(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_429.prn" For Input As #1

For i = 1 To 16

Input #1, em_429(i), Value_429(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_441.prn" For Input As #1

For i = 1 To 15

Input #1, em_441(i), Value_441(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_453.prn" For Input As #1

For i = 1 To 14

Input #1, em_453(i), Value_453(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_465.prn" For Input As #1

```
For i = 1 To 13

    Input #1, em_465(i), Value_465(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_477.prn" For Input As #1

    For i = 1 To 12

        Input #1, em_477(i), Value_477(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_489.prn" For Input As #1

    For i = 1 To 11

        Input #1, em_489(i), Value_489(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_501.prn" For Input As #1

    For i = 1 To 10

        Input #1, em_501(i), Value_501(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_513.prn" For Input As #1

    For i = 1 To 9

        Input #1, em_513(i), Value_513(i)

    Next i
```

Close #1

Open "c:\SFStoolkit\ex_525.prn" For Input As #1

For i = 1 To 8

Input #1, em_525(i), Value_525(i)

Next i

Close #1

'=====

'To Remove Scatters

For i = 1 To size225 - 1

If (Value_225(i + 1) - Value_225(i)) > 12 Then

Value_225(i + 1) = Value_225(i)

Else

Value_225(i) = Value_225(i)

End If

Next i

For i = 1 To size237 - 1

If (Value_237(i + 1) - Value_237(i)) > 12 Then

Value_237(i + 1) = Value_237(i)

Else

Value_237(i) = Value_237(i)

End If

Next i

```
For i = 1 To size249 - 1

    If (Value_249(i + 1) - Value_249(i)) > 12 Then

        Value_249(i + 1) = Value_249(i)

    Else

        Value_249(i) = Value_249(i)

    End If

Next i

For i = 1 To size261 - 1

    If (Value_261(i + 1) - Value_261(i)) > 12 Then

        Value_261(i + 1) = Value_261(i)

    Else

        Value_261(i) = Value_261(i)

    End If

Next i

For i = 1 To size273 - 1

    If (Value_273(i + 1) - Value_273(i)) > 12 Then

        Value_273(i + 1) = Value_273(i)

    Else

        Value_273(i) = Value_273(i)

    End If

Next i

For i = 1 To size285 - 1

    If (Value_285(i + 1) - Value_285(i)) > 12 Then
```

```

    Value_285(i + 1) = Value_285(i)

Else

    Value_285(i) = Value_285(i)

End If

Next i

For i = 1 To size297 - 1

    If (Value_297(i + 1) - Value_297(i)) > 12 Then

        Value_297(i + 1) = Value_297(i)

    Else

        Value_297(i) = Value_297(i)

    End If

Next i

For i = 1 To size309 - 1

    If (Value_309(i + 1) - Value_309(i)) > 12 Then

        Value_309(i + 1) = Value_309(i)

    Else

        Value_309(i) = Value_309(i)

    End If

Next i

For i = 1 To size321 - 1

    If (Value_321(i + 1) - Value_321(i)) > 12 Then

        Value_321(i + 1) = Value_321(i)

    Else

```


Value_321(i) = Value_321(i)

End If

Next i

For i = 1 To size333 - 1

If (Value_333(i + 1) - Value_333(i)) > 12 Then

Value_333(i + 1) = Value_333(i)

Else

Value_333(i) = Value_333(i)

End If

Next i

For i = 1 To size345 - 1

If (Value_345(i + 1) - Value_345(i)) > 12 Then

Value_345(i + 1) = Value_345(i)

Else

Value_345(i) = Value_345(i)

End If

Next i

For i = 1 To size357 - 1

If (Value_357(i + 1) - Value_357(i)) > 12 Then

Value_357(i + 1) = Value_357(i)

Else

Value_357(i) = Value_357(i)

End If

```
Next i

For i = 1 To size369 - 1

    If (Value_369(i + 1) - Value_369(i)) > 12 Then

        Value_369(i + 1) = Value_369(i)

    Else

        Value_369(i) = Value_369(i)

    End If

Next i

For i = 1 To size381 - 1

    If (Value_381(i + 1) - Value_381(i)) > 12 Then

        Value_381(i + 1) = Value_381(i)

    Else

        Value_381(i) = Value_381(i)

    End If

Next i

For i = 1 To size393 - 1

    If (Value_393(i + 1) - Value_393(i)) > 12 Then

        Value_393(i + 1) = Value_393(i)

    Else

        Value_393(i) = Value_393(i)

    End If

Next i
```

For i = 1 To size405 - 1

 If (Value_405(i + 1) - Value_405(i)) > 12 Then

 Value_405(i + 1) = Value_405(i)

 Else

 Value_405(i) = Value_405(i)

 End If

Next i

For i = 1 To size417 - 1

 If (Value_417(i + 1) - Value_417(i)) > 12 Then

 Value_417(i + 1) = Value_417(i)

 Else

 Value_417(i) = Value_417(i)

 End If

Next i

For i = 1 To size429 - 1

 If (Value_429(i + 1) - Value_429(i)) > 12 Then

 Value_429(i + 1) = Value_429(i)

 Else

 Value_429(i) = Value_429(i)

 End If

Next i

For i = 1 To size441 - 1

 If (Value_441(i + 1) - Value_441(i)) > 12 Then

```
Value_441(i + 1) = Value_441(i)

Else

Value_441(i) = Value_441(i)

End If

Next i

For i = 1 To size453 - 1

If (Value_453(i + 1) - Value_453(i)) > 12 Then

Value_453(i + 1) = Value_453(i)

Else

Value_453(i) = Value_453(i)

End If

Next i

For i = 1 To size465 - 1

If (Value_465(i + 1) - Value_465(i)) > 12 Then

Value_465(i + 1) = Value_465(i)

Else

Value_465(i) = Value_465(i)

End If

Next i

For i = 1 To size477 - 1

If (Value_477(i + 1) - Value_477(i)) > 12 Then

Value_477(i + 1) = Value_477(i)

Else
```

Value_477(i) = Value_477(i)

End If

Next i

For i = 1 To size489 - 1

If (Value_489(i + 1) - Value_489(i)) > 12 Then

Value_489(i + 1) = Value_489(i)

Else

Value_489(i) = Value_489(i)

End If

Next i

For i = 1 To size501 - 1

If (Value_501(i + 1) - Value_501(i)) > 12 Then

Value_501(i + 1) = Value_501(i)

Else

Value_501(i) = Value_501(i)

End If

Next i

For i = 1 To size513 - 1

If (Value_513(i + 1) - Value_513(i)) > 12 Then

Value_513(i + 1) = Value_513(i)

Else

Value_513(i) = Value_513(i)

End If

Next i

For i = 1 To size525 - 1

 If (Value_525(i + 1) - Value_525(i)) > 12 Then

 Value_525(i + 1) = Value_525(i)

 Else

 Value_525(i) = Value_525(i)

 End If

Next i

'Computing the Spectral Strip Area

area = Value_225(12) * (388 - 359)

area225 = 0

For i = 1 To size225

 area225 = area225 + 12 * Value_225(i)

Next i

area225 = area225

slopeHPA = ((Abs(Value_225(9) - Value_225(7)) / 24) +

(Abs(Value_237(8) - Value_237(6)) / 24) + _

(Abs(Value_225(10) - Value_225(8)) / 24) + (Abs(Value_237(9) -

Value_237(7)) / 24)) / 4

frmFractionIDHPIA.Show

Let frmFractionIDHPIA.txtSlope.Text = slopeHPA

Let frmFractionIDHPIA.txtArea.Text = area

Let frmFractionIDHPIA.txtSF.Text = slopeHPA * area

End Sub

Private Sub cmdslopeHPIB_Click()

 picResult.Cls

 Dim ex_225(1 To 33, 1 To 2) As Single

 Dim ex_237(1 To 32, 1 To 2) As Single

 Dim ex_249(1 To 31, 1 To 2) As Single

 Dim ex_261(1 To 30, 1 To 2) As Single

 Dim ex_273(1 To 29, 1 To 2) As Single

 Dim ex_285(1 To 28, 1 To 2) As Single

 Dim ex_297(1 To 27, 1 To 2) As Single

 Dim ex_309(1 To 26, 1 To 2) As Single

 Dim ex_321(1 To 25, 1 To 2) As Single

 Dim ex_333(1 To 24, 1 To 2) As Single

 Dim ex_345(1 To 23, 1 To 2) As Single

 Dim ex_357(1 To 22, 1 To 2) As Single

 Dim ex_369(1 To 21, 1 To 2) As Single

 Dim ex_381(1 To 20, 1 To 2) As Single

 Dim ex_393(1 To 19, 1 To 2) As Single

 Dim ex_405(1 To 18, 1 To 2) As Single

 Dim ex_417(1 To 17, 1 To 2) As Single

 Dim ex_429(1 To 16, 1 To 2) As Single

 Dim ex_441(1 To 15, 1 To 2) As Single

 Dim ex_453(1 To 14, 1 To 2) As Single

Dim ex_465(1 To 13, 1 To 2) As Single

Dim ex_477(1 To 12, 1 To 2) As Single

Dim ex_489(1 To 11, 1 To 2) As Single

Dim ex_501(1 To 10, 1 To 2) As Single

Dim ex_513(1 To 9, 1 To 2) As Single

Dim ex_525(1 To 8, 1 To 2) As Single

Dim em_225(1 To 33), em_237(1 To 32), em_249(1 To 31),

em_261(1 To 30), _

em_273(1 To 29), em_285(1 To 28), em_297(1 To 27),

em_309(1 To 26), _

em_321(1 To 25), em_333(1 To 24), em_345(1 To 23),

em_357(1 To 22), _

em_369(1 To 21), em_381(1 To 20), em_393(1 To 19),

em_405(1 To 18), _

em_417(1 To 17), em_429(1 To 16), em_441(1 To 15),

em_453(1 To 14), _

em_465(1 To 13), em_477(1 To 12), em_489(1 To 11),

em_501(1 To 10), _

em_513(1 To 9), em_525(1 To 8) As Integer

Dim Value_225(1 To 33), Value_237(1 To 32), Value_249(1 To

31), Value_261(1 To 30), _

Value_273(1 To 29), Value_285(1 To 28), Value_297(1 To 27),

Value_309(1 To 26), _

Value_321(1 To 25), Value_333(1 To 24), Value_345(1 To 23),
 Value_357(1 To 22), _
 Value_369(1 To 21), Value_381(1 To 20), Value_393(1 To 19),
 Value_405(1 To 18), _
 Value_417(1 To 17), Value_429(1 To 16), Value_441(1 To 15),
 Value_453(1 To 14), _
 Value_465(1 To 13), Value_477(1 To 12), Value_489(1 To 11),
 Value_501(1 To 10), _
 Value_513(1 To 9), Value_525(1 To 8), slopeHPOB As Single
 Dim size225, size237, size249, size261, size273, size285,
 size297, _
 size309, size321, size333, size345, size357, size369, size381, _
 size393, size405, size417, size429, size441, size453, size465, _
 size477, size489, size501, size513, size525 As Integer
 size225 = 33
 size237 = 32
 size249 = 31
 size261 = 30
 size273 = 29
 size285 = 28
 size297 = 27
 size309 = 26
 size321 = 25

size333 = 24

size345 = 23

size357 = 22

size369 = 21

size381 = 20

size393 = 19

size405 = 18

size417 = 17

size429 = 16

size441 = 15

size453 = 14

size465 = 13

size477 = 12

size489 = 11

size501 = 10

size513 = 9

size525 = 8

Open "c:\SFStoolkit\ex_225.prn" For Input As #1

For i = 1 To 33

Input #1, em_225(i), Value_225(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_237.prn" For Input As #1

```
For i = 1 To 32

    Input #1, em_237(i), Value_237(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_249.prn" For Input As #1

    For i = 1 To 31

        Input #1, em_249(i), Value_249(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_261.prn" For Input As #1

    For i = 1 To 30

        Input #1, em_261(i), Value_261(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_273.prn" For Input As #1

    For i = 1 To 29

        Input #1, em_273(i), Value_273(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_285.prn" For Input As #1

    For i = 1 To 28

        Input #1, em_285(i), Value_285(i)

    Next i
```

Close #1

Open "c:\SFStoolkit\ex_297.prn" For Input As #1

For i = 1 To 27

Input #1, em_297(i), Value_297(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_309.prn" For Input As #1

For i = 1 To 26

Input #1, em_309(i), Value_309(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_321.prn" For Input As #1

For i = 1 To 25

Input #1, em_321(i), Value_321(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_333.prn" For Input As #1

For i = 1 To 24

Input #1, em_333(i), Value_333(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_345.prn" For Input As #1

```
For i = 1 To 23

    Input #1, em_345(i), Value_345(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_357.prn" For Input As #1

    For i = 1 To 22

        Input #1, em_357(i), Value_357(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_369.prn" For Input As #1

    For i = 1 To 21

        Input #1, em_369(i), Value_369(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_381.prn" For Input As #1

    For i = 1 To 20

        Input #1, em_381(i), Value_381(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_393.prn" For Input As #1

    For i = 1 To 19

        Input #1, em_393(i), Value_393(i)

    Next i
```

Close #1

Open "c:\SFStoolkit\ex_405.prn" For Input As #1

For i = 1 To 18

Input #1, em_405(i), Value_405(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_417.prn" For Input As #1

For i = 1 To 17

Input #1, em_417(i), Value_417(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_429.prn" For Input As #1

For i = 1 To 16

Input #1, em_429(i), Value_429(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_441.prn" For Input As #1

For i = 1 To 15

Input #1, em_441(i), Value_441(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_453.prn" For Input As #1

```
For i = 1 To 14

    Input #1, em_453(i), Value_453(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_465.prn" For Input As #1

    For i = 1 To 13

        Input #1, em_465(i), Value_465(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_477.prn" For Input As #1

    For i = 1 To 12

        Input #1, em_477(i), Value_477(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_489.prn" For Input As #1

    For i = 1 To 11

        Input #1, em_489(i), Value_489(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_501.prn" For Input As #1

    For i = 1 To 10

        Input #1, em_501(i), Value_501(i)

    Next i
```

Close #1

Open "c:\SFStoolkit\ex_513.prn" For Input As #1

For i = 1 To 9

Input #1, em_513(i), Value_513(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_525.prn" For Input As #1

For i = 1 To 8

Input #1, em_525(i), Value_525(i)

Next i

Close #1

'=====

'To Remove Scatters

For i = 1 To size225 - 1

If (Value_225(i + 1) - Value_225(i)) > 12 Then

Value_225(i + 1) = Value_225(i)

Else

Value_225(i) = Value_225(i)

End If

Next i

For i = 1 To size237 - 1

If (Value_237(i + 1) - Value_237(i)) > 12 Then

Value_237(i + 1) = Value_237(i)


```
Else

    Value_237(i) = Value_237(i)

End If

Next i

For i = 1 To size249 - 1

    If (Value_249(i + 1) - Value_249(i)) > 12 Then

        Value_249(i + 1) = Value_249(i)

    Else

        Value_249(i) = Value_249(i)

    End If

Next i

For i = 1 To size261 - 1

    If (Value_261(i + 1) - Value_261(i)) > 12 Then

        Value_261(i + 1) = Value_261(i)

    Else

        Value_261(i) = Value_261(i)

    End If

Next i

For i = 1 To size273 - 1

    If (Value_273(i + 1) - Value_273(i)) > 12 Then

        Value_273(i + 1) = Value_273(i)

    Else

        Value_273(i) = Value_273(i)
```

```
End If

Next i

For i = 1 To size285 - 1

    If (Value_285(i + 1) - Value_285(i)) > 12 Then

        Value_285(i + 1) = Value_285(i)

    Else

        Value_285(i) = Value_285(i)

    End If

Next i

For i = 1 To size297 - 1

    If (Value_297(i + 1) - Value_297(i)) > 12 Then

        Value_297(i + 1) = Value_297(i)

    Else

        Value_297(i) = Value_297(i)

    End If

Next i

For i = 1 To size309 - 1

    If (Value_309(i + 1) - Value_309(i)) > 12 Then

        Value_309(i + 1) = Value_309(i)

    Else

        Value_309(i) = Value_309(i)

    End If

Next i
```

```
For i = 1 To size321 - 1

    If (Value_321(i + 1) - Value_321(i)) > 12 Then

        Value_321(i + 1) = Value_321(i)

    Else

        Value_321(i) = Value_321(i)

    End If

Next i

For i = 1 To size333 - 1

    If (Value_333(i + 1) - Value_333(i)) > 12 Then

        Value_333(i + 1) = Value_333(i)

    Else

        Value_333(i) = Value_333(i)

    End If

Next i

For i = 1 To size345 - 1

    If (Value_345(i + 1) - Value_345(i)) > 12 Then

        Value_345(i + 1) = Value_345(i)

    Else

        Value_345(i) = Value_345(i)

    End If

Next i

For i = 1 To size357 - 1

    If (Value_357(i + 1) - Value_357(i)) > 12 Then
```

Value_357(i + 1) = Value_357(i)

Else

Value_357(i) = Value_357(i)

End If

Next i

For i = 1 To size369 - 1

If (Value_369(i + 1) - Value_369(i)) > 12 Then

Value_369(i + 1) = Value_369(i)

Else

Value_369(i) = Value_369(i)

End If

Next i

For i = 1 To size381 - 1

If (Value_381(i + 1) - Value_381(i)) > 12 Then

Value_381(i + 1) = Value_381(i)

Else

Value_381(i) = Value_381(i)

End If

Next i

For i = 1 To size393 - 1

If (Value_393(i + 1) - Value_393(i)) > 12 Then

Value_393(i + 1) = Value_393(i)

Else

Value_393(i) = Value_393(i)

End If

Next i

For i = 1 To size405 - 1

If (Value_405(i + 1) - Value_405(i)) > 12 Then

Value_405(i + 1) = Value_405(i)

Else

Value_405(i) = Value_405(i)

End If

Next i

For i = 1 To size417 - 1

If (Value_417(i + 1) - Value_417(i)) > 12 Then

Value_417(i + 1) = Value_417(i)

Else

Value_417(i) = Value_417(i)

End If

Next i

For i = 1 To size429 - 1

If (Value_429(i + 1) - Value_429(i)) > 12 Then

Value_429(i + 1) = Value_429(i)

Else

Value_429(i) = Value_429(i)

End If

Next i

For i = 1 To size441 - 1

 If (Value_441(i + 1) - Value_441(i)) > 12 Then

 Value_441(i + 1) = Value_441(i)

 Else

 Value_441(i) = Value_441(i)

 End If

Next i

For i = 1 To size453 - 1

 If (Value_453(i + 1) - Value_453(i)) > 12 Then

 Value_453(i + 1) = Value_453(i)

 Else

 Value_453(i) = Value_453(i)

 End If

Next i

For i = 1 To size465 - 1

 If (Value_465(i + 1) - Value_465(i)) > 12 Then

 Value_465(i + 1) = Value_465(i)

 Else

 Value_465(i) = Value_465(i)

 End If

Next i

```
For i = 1 To size477 - 1

    If (Value_477(i + 1) - Value_477(i)) > 12 Then

        Value_477(i + 1) = Value_477(i)

    Else

        Value_477(i) = Value_477(i)

    End If

Next i

For i = 1 To size489 - 1

    If (Value_489(i + 1) - Value_489(i)) > 12 Then

        Value_489(i + 1) = Value_489(i)

    Else

        Value_489(i) = Value_489(i)

    End If

Next i

For i = 1 To size501 - 1

    If (Value_501(i + 1) - Value_501(i)) > 12 Then

        Value_501(i + 1) = Value_501(i)

    Else

        Value_501(i) = Value_501(i)

    End If

Next i

For i = 1 To size513 - 1

    If (Value_513(i + 1) - Value_513(i)) > 12 Then
```

```

    Value_513(i + 1) = Value_513(i)

Else

    Value_513(i) = Value_513(i)

End If

Next i

For i = 1 To size525 - 1

    If (Value_525(i + 1) - Value_525(i)) > 12 Then

        Value_525(i + 1) = Value_525(i)

    Else

        Value_525(i) = Value_525(i)

    End If

Next i

'Computing the Spectral Strip Area

area = Value_225(11) * (379 - 355)

area225 = 0

For i = 1 To size225

    area225 = area225 + 12 * Value_225(i)

Next i

area225 = area225

slopeHPB = ((Abs(Value_225(10) - Value_225(8)) / 24) +
(Abs(Value_237(9) - Value_237(7)) / 24) + _
(Abs(Value_225(11) - Value_225(9)) / 24) + (Abs(Value_237(10)
- Value_237(8)) / 24)) / 4

```



```
frmFractionIDHPIB.Show
```

```
Let frmFractionIDHPIB.txtSlope.Text = slopeHPB
```

```
Let frmFractionIDHPIB.txtArea.Text = area
```

```
Let frmFractionIDHPIB.txtSF.Text = slopeHPB * area
```

```
End Sub
```

```
Private Sub cmdslopeHPIN_Click()
```

```
    picResult.Cls
```

```
    Dim ex_225(1 To 33, 1 To 2) As Single
```

```
    Dim ex_237(1 To 32, 1 To 2) As Single
```

```
    Dim ex_249(1 To 31, 1 To 2) As Single
```

```
    Dim ex_261(1 To 30, 1 To 2) As Single
```

```
    Dim ex_273(1 To 29, 1 To 2) As Single
```

```
    Dim ex_285(1 To 28, 1 To 2) As Single
```

```
    Dim ex_297(1 To 27, 1 To 2) As Single
```

```
    Dim ex_309(1 To 26, 1 To 2) As Single
```

```
    Dim ex_321(1 To 25, 1 To 2) As Single
```

```
    Dim ex_333(1 To 24, 1 To 2) As Single
```

```
    Dim ex_345(1 To 23, 1 To 2) As Single
```

```
    Dim ex_357(1 To 22, 1 To 2) As Single
```

```
    Dim ex_369(1 To 21, 1 To 2) As Single
```

```
    Dim ex_381(1 To 20, 1 To 2) As Single
```

```
    Dim ex_393(1 To 19, 1 To 2) As Single
```

```
    Dim ex_405(1 To 18, 1 To 2) As Single
```

Dim ex_417(1 To 17, 1 To 2) As Single
 Dim ex_429(1 To 16, 1 To 2) As Single
 Dim ex_441(1 To 15, 1 To 2) As Single
 Dim ex_453(1 To 14, 1 To 2) As Single
 Dim ex_465(1 To 13, 1 To 2) As Single
 Dim ex_477(1 To 12, 1 To 2) As Single
 Dim ex_489(1 To 11, 1 To 2) As Single
 Dim ex_501(1 To 10, 1 To 2) As Single
 Dim ex_513(1 To 9, 1 To 2) As Single
 Dim ex_525(1 To 8, 1 To 2) As Single
 Dim em_225(1 To 33), em_237(1 To 32), em_249(1 To 31),
 em_261(1 To 30), _
 em_273(1 To 29), em_285(1 To 28), em_297(1 To 27),
 em_309(1 To 26), _
 em_321(1 To 25), em_333(1 To 24), em_345(1 To 23),
 em_357(1 To 22), _
 em_369(1 To 21), em_381(1 To 20), em_393(1 To 19),
 em_405(1 To 18), _
 em_417(1 To 17), em_429(1 To 16), em_441(1 To 15),
 em_453(1 To 14), _
 em_465(1 To 13), em_477(1 To 12), em_489(1 To 11),
 em_501(1 To 10), _
 em_513(1 To 9), em_525(1 To 8) As Integer

```

Dim Value_225(1 To 33), Value_237(1 To 32), Value_249(1 To
31), Value_261(1 To 30), _
Value_273(1 To 29), Value_285(1 To 28), Value_297(1 To 27),
Value_309(1 To 26), _
Value_321(1 To 25), Value_333(1 To 24), Value_345(1 To 23),
Value_357(1 To 22), _
Value_369(1 To 21), Value_381(1 To 20), Value_393(1 To 19),
Value_405(1 To 18), _
Value_417(1 To 17), Value_429(1 To 16), Value_441(1 To 15),
Value_453(1 To 14), _
Value_465(1 To 13), Value_477(1 To 12), Value_489(1 To 11),
Value_501(1 To 10), _
Value_513(1 To 9), Value_525(1 To 8), slopeHPOB As Single
Dim size225, size237, size249, size261, size273, size285,
size297, _
size309, size321, size333, size345, size357, size369, size381, _
size393, size405, size417, size429, size441, size453, size465, _
size477, size489, size501, size513, size525 As Integer

size225 = 33

size237 = 32

size249 = 31

size261 = 30

size273 = 29

```

size285 = 28

size297 = 27

size309 = 26

size321 = 25

size333 = 24

size345 = 23

size357 = 22

size369 = 21

size381 = 20

size393 = 19

size405 = 18

size417 = 17

size429 = 16

size441 = 15

size453 = 14

size465 = 13

size477 = 12

size489 = 11

size501 = 10

size513 = 9

size525 = 8

Open "c:\SFStoolkit\ex_225.prn" For Input As #1

```
For i = 1 To 33

    Input #1, em_225(i), Value_225(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_237.prn" For Input As #1

For i = 1 To 32

    Input #1, em_237(i), Value_237(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_249.prn" For Input As #1

For i = 1 To 31

    Input #1, em_249(i), Value_249(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_261.prn" For Input As #1

For i = 1 To 30

    Input #1, em_261(i), Value_261(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_273.prn" For Input As #1

For i = 1 To 29

    Input #1, em_273(i), Value_273(i)

Next i
```

Close #1

Open "c:\SFStoolkit\ex_285.prn" For Input As #1

For i = 1 To 28

Input #1, em_285(i), Value_285(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_297.prn" For Input As #1

For i = 1 To 27

Input #1, em_297(i), Value_297(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_309.prn" For Input As #1

For i = 1 To 26

Input #1, em_309(i), Value_309(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_321.prn" For Input As #1

For i = 1 To 25

Input #1, em_321(i), Value_321(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_333.prn" For Input As #1

```
For i = 1 To 24

    Input #1, em_333(i), Value_333(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_345.prn" For Input As #1

    For i = 1 To 23

        Input #1, em_345(i), Value_345(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_357.prn" For Input As #1

    For i = 1 To 22

        Input #1, em_357(i), Value_357(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_369.prn" For Input As #1

    For i = 1 To 21

        Input #1, em_369(i), Value_369(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_381.prn" For Input As #1

    For i = 1 To 20

        Input #1, em_381(i), Value_381(i)

    Next i
```

Close #1

Open "c:\SFStoolkit\ex_393.prn" For Input As #1

For i = 1 To 19

Input #1, em_393(i), Value_393(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_405.prn" For Input As #1

For i = 1 To 18

Input #1, em_405(i), Value_405(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_417.prn" For Input As #1

For i = 1 To 17

Input #1, em_417(i), Value_417(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_429.prn" For Input As #1

For i = 1 To 16

Input #1, em_429(i), Value_429(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_441.prn" For Input As #1


```
For i = 1 To 15

    Input #1, em_441(i), Value_441(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_453.prn" For Input As #1

    For i = 1 To 14

        Input #1, em_453(i), Value_453(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_465.prn" For Input As #1

    For i = 1 To 13

        Input #1, em_465(i), Value_465(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_477.prn" For Input As #1

    For i = 1 To 12

        Input #1, em_477(i), Value_477(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_489.prn" For Input As #1

    For i = 1 To 11

        Input #1, em_489(i), Value_489(i)

    Next i
```

Close #1

Open "c:\SFStoolkit\ex_501.prm" For Input As #1

For i = 1 To 10

Input #1, em_501(i), Value_501(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_513.prm" For Input As #1

For i = 1 To 9

Input #1, em_513(i), Value_513(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_525.prm" For Input As #1

For i = 1 To 8

Input #1, em_525(i), Value_525(i)

Next i

Close #1

'To Remove Scatters

For i = 1 To size225 - 1

If (Value_225(i + 1) - Value_225(i)) > 12 Then

Value_225(i + 1) = Value_225(i)

Else

Value_225(i) = Value_225(i)

End If

Next i

For i = 1 To size237 - 1

If (Value_237(i + 1) - Value_237(i)) > 12 Then

Value_237(i + 1) = Value_237(i)

Else

Value_237(i) = Value_237(i)

End If

Next i

For i = 1 To size249 - 1

If (Value_249(i + 1) - Value_249(i)) > 12 Then

Value_249(i + 1) = Value_249(i)

Else

Value_249(i) = Value_249(i)

End If

Next i

For i = 1 To size261 - 1

If (Value_261(i + 1) - Value_261(i)) > 12 Then

Value_261(i + 1) = Value_261(i)

Else

Value_261(i) = Value_261(i)

End If

Next i

```
For i = 1 To size273 - 1

    If (Value_273(i + 1) - Value_273(i)) > 12 Then

        Value_273(i + 1) = Value_273(i)

    Else

        Value_273(i) = Value_273(i)

    End If

Next i

For i = 1 To size285 - 1

    If (Value_285(i + 1) - Value_285(i)) > 12 Then

        Value_285(i + 1) = Value_285(i)

    Else

        Value_285(i) = Value_285(i)

    End If

Next i

For i = 1 To size297 - 1

    If (Value_297(i + 1) - Value_297(i)) > 12 Then

        Value_297(i + 1) = Value_297(i)

    Else

        Value_297(i) = Value_297(i)

    End If

Next i

For i = 1 To size309 - 1

    If (Value_309(i + 1) - Value_309(i)) > 12 Then
```

```
Value_309(i + 1) = Value_309(i)

Else

Value_309(i) = Value_309(i)

End If

Next i

For i = 1 To size321 - 1

If (Value_321(i + 1) - Value_321(i)) > 12 Then

Value_321(i + 1) = Value_321(i)

Else

Value_321(i) = Value_321(i)

End If

Next i

For i = 1 To size333 - 1

If (Value_333(i + 1) - Value_333(i)) > 12 Then

Value_333(i + 1) = Value_333(i)

Else

Value_333(i) = Value_333(i)

End If

Next i

For i = 1 To size345 - 1

If (Value_345(i + 1) - Value_345(i)) > 12 Then

Value_345(i + 1) = Value_345(i)

Else
```

Value_345(i) = Value_345(i)

End If

Next i

For i = 1 To size357 - 1

If (Value_357(i + 1) - Value_357(i)) > 12 Then

Value_357(i + 1) = Value_357(i)

Else

Value_357(i) = Value_357(i)

End If

Next i

For i = 1 To size369 - 1

If (Value_369(i + 1) - Value_369(i)) > 12 Then

Value_369(i + 1) = Value_369(i)

Else

Value_369(i) = Value_369(i)

End If

Next i

For i = 1 To size381 - 1

If (Value_381(i + 1) - Value_381(i)) > 12 Then

Value_381(i + 1) = Value_381(i)

Else

Value_381(i) = Value_381(i)

End If

```
Next i

For i = 1 To size393 - 1

    If (Value_393(i + 1) - Value_393(i)) > 12 Then

        Value_393(i + 1) = Value_393(i)

    Else

        Value_393(i) = Value_393(i)

    End If

Next i

For i = 1 To size405 - 1

    If (Value_405(i + 1) - Value_405(i)) > 12 Then

        Value_405(i + 1) = Value_405(i)

    Else

        Value_405(i) = Value_405(i)

    End If

Next i

For i = 1 To size417 - 1

    If (Value_417(i + 1) - Value_417(i)) > 12 Then

        Value_417(i + 1) = Value_417(i)

    Else

        Value_417(i) = Value_417(i)

    End If

Next i
```

```

For i = 1 To size429 - 1

    If (Value_429(i + 1) - Value_429(i)) > 12 Then

        Value_429(i + 1) = Value_429(i)

    Else

        Value_429(i) = Value_429(i)

    End If

Next i

For i = 1 To size441 - 1

    If (Value_441(i + 1) - Value_441(i)) > 12 Then

        Value_441(i + 1) = Value_441(i)

    Else

        Value_441(i) = Value_441(i)

    End If

Next i

For i = 1 To size453 - 1

    If (Value_453(i + 1) - Value_453(i)) > 12 Then

        Value_453(i + 1) = Value_453(i)

    Else

        Value_453(i) = Value_453(i)

    End If

Next i

For i = 1 To size465 - 1

    If (Value_465(i + 1) - Value_465(i)) > 12 Then

```


Value_465(i + 1) = Value_465(i)

Else

Value_465(i) = Value_465(i)

End If

Next i

For i = 1 To size477 - 1

If (Value_477(i + 1) - Value_477(i)) > 12 Then

Value_477(i + 1) = Value_477(i)

Else

Value_477(i) = Value_477(i)

End If

Next i

For i = 1 To size489 - 1

If (Value_489(i + 1) - Value_489(i)) > 12 Then

Value_489(i + 1) = Value_489(i)

Else

Value_489(i) = Value_489(i)

End If

Next i

For i = 1 To size501 - 1

If (Value_501(i + 1) - Value_501(i)) > 12 Then

Value_501(i + 1) = Value_501(i)

Else

```

    Value_501(i) = Value_501(i)

End If

Next i

For i = 1 To size513 - 1

    If (Value_513(i + 1) - Value_513(i)) > 12 Then

        Value_513(i + 1) = Value_513(i)

    Else

        Value_513(i) = Value_513(i)

    End If

Next i

For i = 1 To size525 - 1

    If (Value_525(i + 1) - Value_525(i)) > 12 Then

        Value_525(i + 1) = Value_525(i)

    Else

        Value_525(i) = Value_525(i)

    End If

Next i

'Computing the Spectral Strip area

area = Value_225(30) * (600 - 592)

area225 = 0

For i = 1 To size225

    area225 = area225 + 12 * Value_225(i)

Next i

```

```

    area225 = area225

    slopeHPN = ((Abs(Value_225(31) - Value_225(29)) / 24) +
    (Abs(Value_225(32) - Value_225(30)) / 24)) / 2

    frmFractionIDHPIN.Show

    Let frmFractionIDHPIN.txtSlope.Text = slopeHPN

    Let frmFractionIDHPIN.txtArea.Text = area

    Let frmFractionIDHPIN.txtSF.Text = slopeHPN * area

End Sub

Private Sub cmdslopeHPOA_Click()

    picResult.Cls

    Dim ex_225(1 To 33, 1 To 2) As Single
    Dim ex_237(1 To 32, 1 To 2) As Single
    Dim ex_249(1 To 31, 1 To 2) As Single
    Dim ex_261(1 To 30, 1 To 2) As Single
    Dim ex_273(1 To 29, 1 To 2) As Single
    Dim ex_285(1 To 28, 1 To 2) As Single
    Dim ex_297(1 To 27, 1 To 2) As Single
    Dim ex_309(1 To 26, 1 To 2) As Single
    Dim ex_321(1 To 25, 1 To 2) As Single
    Dim ex_333(1 To 24, 1 To 2) As Single
    Dim ex_345(1 To 23, 1 To 2) As Single
    Dim ex_357(1 To 22, 1 To 2) As Single
    Dim ex_369(1 To 21, 1 To 2) As Single

```

Dim ex_381(1 To 20, 1 To 2) As Single
 Dim ex_393(1 To 19, 1 To 2) As Single
 Dim ex_405(1 To 18, 1 To 2) As Single
 Dim ex_417(1 To 17, 1 To 2) As Single
 Dim ex_429(1 To 16, 1 To 2) As Single
 Dim ex_441(1 To 15, 1 To 2) As Single
 Dim ex_453(1 To 14, 1 To 2) As Single
 Dim ex_465(1 To 13, 1 To 2) As Single
 Dim ex_477(1 To 12, 1 To 2) As Single
 Dim ex_489(1 To 11, 1 To 2) As Single
 Dim ex_501(1 To 10, 1 To 2) As Single
 Dim ex_513(1 To 9, 1 To 2) As Single
 Dim ex_525(1 To 8, 1 To 2) As Single
 Dim em_225(1 To 33), em_237(1 To 32), em_249(1 To 31),
 em_261(1 To 30), _
 em_273(1 To 29), em_285(1 To 28), em_297(1 To 27),
 em_309(1 To 26), _
 em_321(1 To 25), em_333(1 To 24), em_345(1 To 23),
 em_357(1 To 22), _
 em_369(1 To 21), em_381(1 To 20), em_393(1 To 19),
 em_405(1 To 18), _
 em_417(1 To 17), em_429(1 To 16), em_441(1 To 15),
 em_453(1 To 14), _

```

em_465(1 To 13), em_477(1 To 12), em_489(1 To 11),
em_501(1 To 10), _
em_513(1 To 9), em_525(1 To 8) As Integer
Dim Value_225(1 To 33), Value_237(1 To 32), Value_249(1 To
31), Value_261(1 To 30), _
Value_273(1 To 29), Value_285(1 To 28), Value_297(1 To 27),
Value_309(1 To 26), _
Value_321(1 To 25), Value_333(1 To 24), Value_345(1 To 23),
Value_357(1 To 22), _
Value_369(1 To 21), Value_381(1 To 20), Value_393(1 To 19),
Value_405(1 To 18), _
Value_417(1 To 17), Value_429(1 To 16), Value_441(1 To 15),
Value_453(1 To 14), _
Value_465(1 To 13), Value_477(1 To 12), Value_489(1 To 11),
Value_501(1 To 10), _
Value_513(1 To 9), Value_525(1 To 8), slopeHPOB As Single
Dim size225, size237, size249, size261, size273, size285,
size297, _
size309, size321, size333, size345, size357, size369, size381, _
size393, size405, size417, size429, size441, size453, size465, _
size477, size489, size501, size513, size525 As Integer
size225 = 33
size237 = 32

```

$$\text{size249} = 31$$

$$\text{size261} = 30$$

$$\text{size273} = 29$$

$$\text{size285} = 28$$

$$\text{size297} = 27$$

$$\text{size309} = 26$$

$$\text{size321} = 25$$

$$\text{size333} = 24$$

$$\text{size345} = 23$$

$$\text{size357} = 22$$

$$\text{size369} = 21$$

$$\text{size381} = 20$$

$$\text{size393} = 19$$

$$\text{size405} = 18$$

$$\text{size417} = 17$$

$$\text{size429} = 16$$

$$\text{size441} = 15$$

$$\text{size453} = 14$$

$$\text{size465} = 13$$

$$\text{size477} = 12$$

$$\text{size489} = 11$$

$$\text{size501} = 10$$

$$\text{size513} = 9$$

```
size525 = 8

Open "c:\SFStoolkit\ex_225.prn" For Input As #1

For i = 1 To 33

Input #1, em_225(i), Value_225(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_237.prn" For Input As #1

For i = 1 To 32

Input #1, em_237(i), Value_237(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_249.prn" For Input As #1

For i = 1 To 31

Input #1, em_249(i), Value_249(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_261.prn" For Input As #1

For i = 1 To 30

Input #1, em_261(i), Value_261(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_273.prn" For Input As #1
```

```
For i = 1 To 29

    Input #1, em_273(i), Value_273(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_285.prn" For Input As #1

    For i = 1 To 28

        Input #1, em_285(i), Value_285(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_297.prn" For Input As #1

    For i = 1 To 27

        Input #1, em_297(i), Value_297(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_309.prn" For Input As #1

    For i = 1 To 26

        Input #1, em_309(i), Value_309(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_321.prn" For Input As #1

    For i = 1 To 25

        Input #1, em_321(i), Value_321(i)

    Next i
```


Close #1

Open "c:\SFStoolkit\ex_333.prn" For Input As #1

For i = 1 To 24

Input #1, em_333(i), Value_333(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_345.prn" For Input As #1

For i = 1 To 23

Input #1, em_345(i), Value_345(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_357.prn" For Input As #1

For i = 1 To 22

Input #1, em_357(i), Value_357(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_369.prn" For Input As #1

For i = 1 To 21

Input #1, em_369(i), Value_369(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_381.prn" For Input As #1

```
For i = 1 To 20

    Input #1, em_381(i), Value_381(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_393.prn" For Input As #1

    For i = 1 To 19

        Input #1, em_393(i), Value_393(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_405.prn" For Input As #1

    For i = 1 To 18

        Input #1, em_405(i), Value_405(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_417.prn" For Input As #1

    For i = 1 To 17

        Input #1, em_417(i), Value_417(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_429.prn" For Input As #1

    For i = 1 To 16

        Input #1, em_429(i), Value_429(i)

    Next i
```

Close #1

Open "c:\SFStoolkit\ex_441.prn" For Input As #1

For i = 1 To 15

Input #1, em_441(i), Value_441(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_453.prn" For Input As #1

For i = 1 To 14

Input #1, em_453(i), Value_453(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_465.prn" For Input As #1

For i = 1 To 13

Input #1, em_465(i), Value_465(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_477.prn" For Input As #1

For i = 1 To 12

Input #1, em_477(i), Value_477(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_489.prn" For Input As #1

```

For i = 1 To 11

    Input #1, em_489(i), Value_489(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_501.pm" For Input As #1

    For i = 1 To 10

        Input #1, em_501(i), Value_501(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_513.pm" For Input As #1

    For i = 1 To 9

        Input #1, em_513(i), Value_513(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_525.pm" For Input As #1

    For i = 1 To 8

        Input #1, em_525(i), Value_525(i)

    Next i

Close #1

=====

'To Remove Scatters

For i = 1 To size225 - 1

    If (Value_225(i + 1) - Value_225(i)) > 12 Then

```

```
        Value_225(i + 1) = Value_225(i)

    Else

        Value_225(i) = Value_225(i)

    End If

Next i

For i = 1 To size237 - 1

    If (Value_237(i + 1) - Value_237(i)) > 12 Then

        Value_237(i + 1) = Value_237(i)

    Else

        Value_237(i) = Value_237(i)

    End If

Next i

For i = 1 To size249 - 1

    If (Value_249(i + 1) - Value_249(i)) > 12 Then

        Value_249(i + 1) = Value_249(i)

    Else

        Value_249(i) = Value_249(i)

    End If

Next i

For i = 1 To size261 - 1

    If (Value_261(i + 1) - Value_261(i)) > 12 Then

        Value_261(i + 1) = Value_261(i)

    Else
```

```
        Value_261(i) = Value_261(i)

    End If

Next i

For i = 1 To size273 - 1

    If (Value_273(i + 1) - Value_273(i)) > 12 Then

        Value_273(i + 1) = Value_273(i)

    Else

        Value_273(i) = Value_273(i)

    End If

Next i

For i = 1 To size285 - 1

    If (Value_285(i + 1) - Value_285(i)) > 12 Then

        Value_285(i + 1) = Value_285(i)

    Else

        Value_285(i) = Value_285(i)

    End If

Next i

For i = 1 To size297 - 1

    If (Value_297(i + 1) - Value_297(i)) > 12 Then

        Value_297(i + 1) = Value_297(i)

    Else

        Value_297(i) = Value_297(i)

    End If
```

Next i

For i = 1 To size309 - 1

 If (Value_309(i + 1) - Value_309(i)) > 12 Then

 Value_309(i + 1) = Value_309(i)

 Else

 Value_309(i) = Value_309(i)

 End If

Next i

For i = 1 To size321 - 1

 If (Value_321(i + 1) - Value_321(i)) > 12 Then

 Value_321(i + 1) = Value_321(i)

 Else

 Value_321(i) = Value_321(i)

 End If

Next i

For i = 1 To size333 - 1

 If (Value_333(i + 1) - Value_333(i)) > 12 Then

 Value_333(i + 1) = Value_333(i)

 Else

 Value_333(i) = Value_333(i)

 End If

Next i

```
For i = 1 To size345 - 1

    If (Value_345(i + 1) - Value_345(i)) > 12 Then

        Value_345(i + 1) = Value_345(i)

    Else

        Value_345(i) = Value_345(i)

    End If

Next i

For i = 1 To size357 - 1

    If (Value_357(i + 1) - Value_357(i)) > 12 Then

        Value_357(i + 1) = Value_357(i)

    Else

        Value_357(i) = Value_357(i)

    End If

Next i

For i = 1 To size369 - 1

    If (Value_369(i + 1) - Value_369(i)) > 12 Then

        Value_369(i + 1) = Value_369(i)

    Else

        Value_369(i) = Value_369(i)

    End If

Next i

For i = 1 To size381 - 1

    If (Value_381(i + 1) - Value_381(i)) > 12 Then
```



```
Value_381(i + 1) = Value_381(i)

Else

Value_381(i) = Value_381(i)

End If

Next i

For i = 1 To size393 - 1

If (Value_393(i + 1) - Value_393(i)) > 12 Then

Value_393(i + 1) = Value_393(i)

Else

Value_393(i) = Value_393(i)

End If

Next i

For i = 1 To size405 - 1

If (Value_405(i + 1) - Value_405(i)) > 12 Then

Value_405(i + 1) = Value_405(i)

Else

Value_405(i) = Value_405(i)

End If

Next i

For i = 1 To size417 - 1

If (Value_417(i + 1) - Value_417(i)) > 12 Then

Value_417(i + 1) = Value_417(i)

Else
```

```
Value_417(i) = Value_417(i)

End If

Next i

For i = 1 To size429 - 1

    If (Value_429(i + 1) - Value_429(i)) > 12 Then

        Value_429(i + 1) = Value_429(i)

    Else

        Value_429(i) = Value_429(i)

    End If

Next i

For i = 1 To size441 - 1

    If (Value_441(i + 1) - Value_441(i)) > 12 Then

        Value_441(i + 1) = Value_441(i)

    Else

        Value_441(i) = Value_441(i)

    End If

Next i

For i = 1 To size453 - 1

    If (Value_453(i + 1) - Value_453(i)) > 12 Then

        Value_453(i + 1) = Value_453(i)

    Else

        Value_453(i) = Value_453(i)

    End If
```

Next i

For i = 1 To size465 - 1

If (Value_465(i + 1) - Value_465(i)) > 12 Then

Value_465(i + 1) = Value_465(i)

Else

Value_465(i) = Value_465(i)

End If

Next i

For i = 1 To size477 - 1

If (Value_477(i + 1) - Value_477(i)) > 12 Then

Value_477(i + 1) = Value_477(i)

Else

Value_477(i) = Value_477(i)

End If

Next i

For i = 1 To size489 - 1

If (Value_489(i + 1) - Value_489(i)) > 12 Then

Value_489(i + 1) = Value_489(i)

Else

Value_489(i) = Value_489(i)

End If

Next i

```

For i = 1 To size501 - 1

    If (Value_501(i + 1) - Value_501(i)) > 12 Then

        Value_501(i + 1) = Value_501(i)

    Else

        Value_501(i) = Value_501(i)

    End If

Next i

For i = 1 To size513 - 1

    If (Value_513(i + 1) - Value_513(i)) > 12 Then

        Value_513(i + 1) = Value_513(i)

    Else

        Value_513(i) = Value_513(i)

    End If

Next i

For i = 1 To size525 - 1

    If (Value_525(i + 1) - Value_525(i)) > 12 Then

        Value_525(i + 1) = Value_525(i)

    Else

        Value_525(i) = Value_525(i)

    End If

Next i

'Computing the Spectral Strip Area

area = Value_237(12) * (404 - 367)

```

```

area225 = 0

For i = 1 To size225

area225 = area225 + 12 * Value_225(i)

Next i

area225 = area225

slopeHFA = ((Abs(Value_237(14) - Value_237(12)) / 24) +
(Abs(Value_249(13) - Value_249(11)) / 24) + _
(Abs(Value_237(15) - Value_237(13)) / 24) +
(Abs(Value_249(14) - Value_249(12)) / 24)) / 4

frmFractionIDHPOA.Show

Let frmFractionIDHPOA.txtSlope.Text = slopeHFA

Let frmFractionIDHPOA.txtArea.Text = area

Let frmFractionIDHPOA.txtSF.Text = slopeHFA * area

End Sub

Public Sub cmdslopeHPOB_Click()

    picResult.Cls

    Dim ex_225(1 To 33, 1 To 2) As Single

    Dim ex_237(1 To 32, 1 To 2) As Single

    Dim ex_249(1 To 31, 1 To 2) As Single

    Dim ex_261(1 To 30, 1 To 2) As Single

    Dim ex_273(1 To 29, 1 To 2) As Single

    Dim ex_285(1 To 28, 1 To 2) As Single

    Dim ex_297(1 To 27, 1 To 2) As Single

```

Dim ex_309(1 To 26, 1 To 2) As Single
 Dim ex_321(1 To 25, 1 To 2) As Single
 Dim ex_333(1 To 24, 1 To 2) As Single
 Dim ex_345(1 To 23, 1 To 2) As Single
 Dim ex_357(1 To 22, 1 To 2) As Single
 Dim ex_369(1 To 21, 1 To 2) As Single
 Dim ex_381(1 To 20, 1 To 2) As Single
 Dim ex_393(1 To 19, 1 To 2) As Single
 Dim ex_405(1 To 18, 1 To 2) As Single
 Dim ex_417(1 To 17, 1 To 2) As Single
 Dim ex_429(1 To 16, 1 To 2) As Single
 Dim ex_441(1 To 15, 1 To 2) As Single
 Dim ex_453(1 To 14, 1 To 2) As Single
 Dim ex_465(1 To 13, 1 To 2) As Single
 Dim ex_477(1 To 12, 1 To 2) As Single
 Dim ex_489(1 To 11, 1 To 2) As Single
 Dim ex_501(1 To 10, 1 To 2) As Single
 Dim ex_513(1 To 9, 1 To 2) As Single
 Dim ex_525(1 To 8, 1 To 2) As Single
 Dim em_225(1 To 33), em_237(1 To 32), em_249(1 To 31),
 em_261(1 To 30), _
 em_273(1 To 29), em_285(1 To 28), em_297(1 To 27),
 em_309(1 To 26), _

```

em_321(1 To 25), em_333(1 To 24), em_345(1 To 23),
em_357(1 To 22), _
em_369(1 To 21), em_381(1 To 20), em_393(1 To 19),
em_405(1 To 18), _
em_417(1 To 17), em_429(1 To 16), em_441(1 To 15),
em_453(1 To 14), _
em_465(1 To 13), em_477(1 To 12), em_489(1 To 11),
em_501(1 To 10), _
em_513(1 To 9), em_525(1 To 8) As Integer
Dim Value_225(1 To 33), Value_237(1 To 32), Value_249(1 To
31), Value_261(1 To 30), _
Value_273(1 To 29), Value_285(1 To 28), Value_297(1 To 27),
Value_309(1 To 26), _
Value_321(1 To 25), Value_333(1 To 24), Value_345(1 To 23),
Value_357(1 To 22), _
Value_369(1 To 21), Value_381(1 To 20), Value_393(1 To 19),
Value_405(1 To 18), _
Value_417(1 To 17), Value_429(1 To 16), Value_441(1 To 15),
Value_453(1 To 14), _
Value_465(1 To 13), Value_477(1 To 12), Value_489(1 To 11),
Value_501(1 To 10), _
Value_513(1 To 9), Value_525(1 To 8), slopeHPOB As Single

```

Dim size225, size237, size249, size261, size273, size285,
size297, _
size309, size321, size333, size345, size357, size369, size381, _
size393, size405, size417, size429, size441, size453, size465, _
size477, size489, size501, size513, size525 As Integer

size225 = 33

size237 = 32

size249 = 31

size261 = 30

size273 = 29

size285 = 28

size297 = 27

size309 = 26

size321 = 25

size333 = 24

size345 = 23

size357 = 22

size369 = 21

size381 = 20

size393 = 19

size405 = 18

size417 = 17

size429 = 16

size441 = 15

size453 = 14

size465 = 13

size477 = 12

size489 = 11

size501 = 10

size513 = 9

size525 = 8

Open "c:\SFStoolkit\ex_225.prn" For Input As #1

For i = 1 To 33

Input #1, em_225(i), Value_225(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_237.prn" For Input As #1

For i = 1 To 32

Input #1, em_237(i), Value_237(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_249.prn" For Input As #1

For i = 1 To 31

Input #1, em_249(i), Value_249(i)

Next i

Close #1

```
Open "c:\SFStoolkit\ex_261.prn" For Input As #1

  For i = 1 To 30

    Input #1, em_261(i), Value_261(i)

  Next i

Close #1

Open "c:\SFStoolkit\ex_273.prn" For Input As #1

  For i = 1 To 29

    Input #1, em_273(i), Value_273(i)

  Next i

Close #1

Open "c:\SFStoolkit\ex_285.prn" For Input As #1

  For i = 1 To 28

    Input #1, em_285(i), Value_285(i)

  Next i

Close #1

Open "c:\SFStoolkit\ex_297.prn" For Input As #1

  For i = 1 To 27

    Input #1, em_297(i), Value_297(i)

  Next i

Close #1

Open "c:\SFStoolkit\ex_309.prn" For Input As #1

  For i = 1 To 26

    Input #1, em_309(i), Value_309(i)
```

```
Next i

Close #1

Open "c:\SFStoolkit\ex_321.prn" For Input As #1

For i = 1 To 25

Input #1, em_321(i), Value_321(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_333.prn" For Input As #1

For i = 1 To 24

Input #1, em_333(i), Value_333(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_345.prn" For Input As #1

For i = 1 To 23

Input #1, em_345(i), Value_345(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_357.prn" For Input As #1

For i = 1 To 22

Input #1, em_357(i), Value_357(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_369.prn" For Input As #1
```

```
For i = 1 To 21

    Input #1, em_369(i), Value_369(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_381.prn" For Input As #1

    For i = 1 To 20

        Input #1, em_381(i), Value_381(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_393.prn" For Input As #1

    For i = 1 To 19

        Input #1, em_393(i), Value_393(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_405.prn" For Input As #1

    For i = 1 To 18

        Input #1, em_405(i), Value_405(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_417.prn" For Input As #1

    For i = 1 To 17

        Input #1, em_417(i), Value_417(i)

    Next i
```

Close #1

Open "c:\SFStoolkit\ex_429.prn" For Input As #1

For i = 1 To 16

Input #1, em_429(i), Value_429(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_441.prn" For Input As #1

For i = 1 To 15

Input #1, em_441(i), Value_441(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_453.prn" For Input As #1

For i = 1 To 14

Input #1, em_453(i), Value_453(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_465.prn" For Input As #1

For i = 1 To 13

Input #1, em_465(i), Value_465(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_477.prn" For Input As #1

```
For i = 1 To 12

Input #1, em_477(i), Value_477(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_489.prn" For Input As #1

For i = 1 To 11

Input #1, em_489(i), Value_489(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_501.prn" For Input As #1

For i = 1 To 10

Input #1, em_501(i), Value_501(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_513.prn" For Input As #1

For i = 1 To 9

Input #1, em_513(i), Value_513(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_525.prn" For Input As #1

For i = 1 To 8

Input #1, em_525(i), Value_525(i)

Next i
```

Close #1

'To Remove Scatters

For i = 1 To size225 - 1

 If (Value_225(i + 1) - Value_225(i)) > 12 Then

 Value_225(i + 1) = Value_225(i)

 Else

 Value_225(i) = Value_225(i)

 End If

Next i

For i = 1 To size237 - 1

 If (Value_237(i + 1) - Value_237(i)) > 12 Then

 Value_237(i + 1) = Value_237(i)

 Else

 Value_237(i) = Value_237(i)

 End If

Next i

For i = 1 To size249 - 1

 If (Value_249(i + 1) - Value_249(i)) > 12 Then

 Value_249(i + 1) = Value_249(i)

 Else

 Value_249(i) = Value_249(i)

 End If

Next i

For i = 1 To size261 - 1

 If (Value_261(i + 1) - Value_261(i)) > 12 Then

 Value_261(i + 1) = Value_261(i)

 Else

 Value_261(i) = Value_261(i)

 End If

Next i

For i = 1 To size273 - 1

 If (Value_273(i + 1) - Value_273(i)) > 12 Then

 Value_273(i + 1) = Value_273(i)

 Else

 Value_273(i) = Value_273(i)

 End If

Next i

For i = 1 To size285 - 1

 If (Value_285(i + 1) - Value_285(i)) > 12 Then

 Value_285(i + 1) = Value_285(i)

 Else

 Value_285(i) = Value_285(i)

 End If

Next i

For i = 1 To size297 - 1

If (Value_297(i + 1) - Value_297(i)) > 12 Then

Value_297(i + 1) = Value_297(i)

Else

Value_297(i) = Value_297(i)

End If

Next i

For i = 1 To size309 - 1

If (Value_309(i + 1) - Value_309(i)) > 12 Then

Value_309(i + 1) = Value_309(i)

Else

Value_309(i) = Value_309(i)

End If

Next i

For i = 1 To size321 - 1

If (Value_321(i + 1) - Value_321(i)) > 12 Then

Value_321(i + 1) = Value_321(i)

Else

Value_321(i) = Value_321(i)

End If

Next i

For i = 1 To size333 - 1

If (Value_333(i + 1) - Value_333(i)) > 12 Then

Value_333(i + 1) = Value_333(i)

```
Else

    Value_333(i) = Value_333(i)

End If

Next i

For i = 1 To size345 - 1

    If (Value_345(i + 1) - Value_345(i)) > 12 Then

        Value_345(i + 1) = Value_345(i)

    Else

        Value_345(i) = Value_345(i)

    End If

Next i

For i = 1 To size357 - 1

    If (Value_357(i + 1) - Value_357(i)) > 12 Then

        Value_357(i + 1) = Value_357(i)

    Else

        Value_357(i) = Value_357(i)

    End If

Next i

For i = 1 To size369 - 1

    If (Value_369(i + 1) - Value_369(i)) > 12 Then

        Value_369(i + 1) = Value_369(i)

    Else

        Value_369(i) = Value_369(i)

    End If

Next i
```

```
End If

Next i

For i = 1 To size381 - 1

    If (Value_381(i + 1) - Value_381(i)) > 12 Then

        Value_381(i + 1) = Value_381(i)

    Else

        Value_381(i) = Value_381(i)

    End If

Next i

For i = 1 To size393 - 1

    If (Value_393(i + 1) - Value_393(i)) > 12 Then

        Value_393(i + 1) = Value_393(i)

    Else

        Value_393(i) = Value_393(i)

    End If

Next i

For i = 1 To size405 - 1

    If (Value_405(i + 1) - Value_405(i)) > 12 Then

        Value_405(i + 1) = Value_405(i)

    Else

        Value_405(i) = Value_405(i)

    End If

Next i
```

```
For i = 1 To size417 - 1

    If (Value_417(i + 1) - Value_417(i)) > 12 Then

        Value_417(i + 1) = Value_417(i)

    Else

        Value_417(i) = Value_417(i)

    End If

Next i

For i = 1 To size429 - 1

    If (Value_429(i + 1) - Value_429(i)) > 12 Then

        Value_429(i + 1) = Value_429(i)

    Else

        Value_429(i) = Value_429(i)

    End If

Next i

For i = 1 To size441 - 1

    If (Value_441(i + 1) - Value_441(i)) > 12 Then

        Value_441(i + 1) = Value_441(i)

    Else

        Value_441(i) = Value_441(i)

    End If

Next i

For i = 1 To size453 - 1

    If (Value_453(i + 1) - Value_453(i)) > 12 Then
```

Value_453(i + 1) = Value_453(i)

Else

Value_453(i) = Value_453(i)

End If

Next i

For i = 1 To size465 - 1

If (Value_465(i + 1) - Value_465(i)) > 12 Then

Value_465(i + 1) = Value_465(i)

Else

Value_465(i) = Value_465(i)

End If

Next i

For i = 1 To size477 - 1

If (Value_477(i + 1) - Value_477(i)) > 12 Then

Value_477(i + 1) = Value_477(i)

Else

Value_477(i) = Value_477(i)

End If

Next i

For i = 1 To size489 - 1

If (Value_489(i + 1) - Value_489(i)) > 12 Then

Value_489(i + 1) = Value_489(i)

Else

Value_489(i) = Value_489(i)

End If

Next i

For i = 1 To size501 - 1

If (Value_501(i + 1) - Value_501(i)) > 12 Then

Value_501(i + 1) = Value_501(i)

Else

Value_501(i) = Value_501(i)

End If

Next i

For i = 1 To size513 - 1

If (Value_513(i + 1) - Value_513(i)) > 12 Then

Value_513(i + 1) = Value_513(i)

Else

Value_513(i) = Value_513(i)

End If

Next i

For i = 1 To size525 - 1

If (Value_525(i + 1) - Value_525(i)) > 12 Then

Value_525(i + 1) = Value_525(i)

Else

Value_525(i) = Value_525(i)

End If

Next i

'Computing the spectral strip area

area = Value_225(10) * (368 - 340)

area225 = 0

For i = 1 To size225

area225 = area225 + 12 * Value_225(i)

Next i

area225 = area225

slopeHFB = ((Abs(Value_225(11) - Value_225(9)) / 24) +

(Abs(Value_237(5) - Value_237(3)) / 24) + _

(Abs(Value_225(12) - Value_225(10)) / 24) + (Abs(Value_237(6)

- Value_237(4)) / 24)) / 4

frmFractionIDHPOB.Show

Let frmFractionIDHPOB.txtSlope.Text = slopeHFB

Let frmFractionIDHPOB.txtArea.Text = area

Let frmFractionIDHPOB.txtSF.Text = slopeHFB * area

End Sub

Private Sub cmdslopeHPON_Click()

picResult.Cls

Dim ex_225(1 To 33, 1 To 2) As Single

Dim ex_237(1 To 32, 1 To 2) As Single

Dim ex_249(1 To 31, 1 To 2) As Single

Dim ex_261(1 To 30, 1 To 2) As Single
Dim ex_273(1 To 29, 1 To 2) As Single
Dim ex_285(1 To 28, 1 To 2) As Single
Dim ex_297(1 To 27, 1 To 2) As Single
Dim ex_309(1 To 26, 1 To 2) As Single
Dim ex_321(1 To 25, 1 To 2) As Single
Dim ex_333(1 To 24, 1 To 2) As Single
Dim ex_345(1 To 23, 1 To 2) As Single
Dim ex_357(1 To 22, 1 To 2) As Single
Dim ex_369(1 To 21, 1 To 2) As Single
Dim ex_381(1 To 20, 1 To 2) As Single
Dim ex_393(1 To 19, 1 To 2) As Single
Dim ex_405(1 To 18, 1 To 2) As Single
Dim ex_417(1 To 17, 1 To 2) As Single
Dim ex_429(1 To 16, 1 To 2) As Single
Dim ex_441(1 To 15, 1 To 2) As Single
Dim ex_453(1 To 14, 1 To 2) As Single
Dim ex_465(1 To 13, 1 To 2) As Single
Dim ex_477(1 To 12, 1 To 2) As Single
Dim ex_489(1 To 11, 1 To 2) As Single
Dim ex_501(1 To 10, 1 To 2) As Single
Dim ex_513(1 To 9, 1 To 2) As Single
Dim ex_525(1 To 8, 1 To 2) As Single


```

Dim em_225(1 To 33), em_237(1 To 32), em_249(1 To 31),
em_261(1 To 30), _
em_273(1 To 29), em_285(1 To 28), em_297(1 To 27),
em_309(1 To 26), _
em_321(1 To 25), em_333(1 To 24), em_345(1 To 23),
em_357(1 To 22), _
em_369(1 To 21), em_381(1 To 20), em_393(1 To 19),
em_405(1 To 18), _
em_417(1 To 17), em_429(1 To 16), em_441(1 To 15),
em_453(1 To 14), _
em_465(1 To 13), em_477(1 To 12), em_489(1 To 11),
em_501(1 To 10), _
em_513(1 To 9), em_525(1 To 8) As Integer

```

```

Dim Value_225(1 To 33), Value_237(1 To 32), Value_249(1 To
31), Value_261(1 To 30), _
Value_273(1 To 29), Value_285(1 To 28), Value_297(1 To 27),
Value_309(1 To 26), _
Value_321(1 To 25), Value_333(1 To 24), Value_345(1 To 23),
Value_357(1 To 22), _
Value_369(1 To 21), Value_381(1 To 20), Value_393(1 To 19),
Value_405(1 To 18), _

```

Value_417(1 To 17), Value_429(1 To 16), Value_441(1 To 15),
 Value_453(1 To 14), _
 Value_465(1 To 13), Value_477(1 To 12), Value_489(1 To 11),
 Value_501(1 To 10), _
 Value_513(1 To 9), Value_525(1 To 8), slopeHPOB As Single
 Dim size225, size237, size249, size261, size273, size285, s
 size297, _
 size309, size321, size333, size345, size357, size369, size381, _
 size393, size405, size417, size429, size441, size453, size465, _
 size477, size489, size501, size513, size525 As Integer

 size225 = 33

 size237 = 32

 size249 = 31

 size261 = 30

 size273 = 29

 size285 = 28

 size297 = 27

 size309 = 26

 size321 = 25

 size333 = 24

 size345 = 23

 size357 = 22

 size369 = 21

```
size381 = 20

size393 = 19

size405 = 18

size417 = 17

size429 = 16

size441 = 15

size453 = 14

size465 = 13

size477 = 12

size489 = 11

size501 = 10

size513 = 9

size525 = 8

Open "c:\SFStoolkit\ex_225.prn" For Input As #1

For i = 1 To 33

    Input #1, em_225(i), Value_225(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_237.prn" For Input As #1

For i = 1 To 32

    Input #1, em_237(i), Value_237(i)

Next i

Close #1
```

```
Open "c:\SFStoolkit\ex_249.prn" For Input As #1

  For i = 1 To 31

    Input #1, em_249(i), Value_249(i)

  Next i

Close #1

Open "c:\SFStoolkit\ex_261.prn" For Input As #1

  For i = 1 To 30

    Input #1, em_261(i), Value_261(i)

  Next i

Close #1

Open "c:\SFStoolkit\ex_273.prn" For Input As #1

  For i = 1 To 29

    Input #1, em_273(i), Value_273(i)

  Next i

Close #1

Open "c:\SFStoolkit\ex_285.prn" For Input As #1

  For i = 1 To 28

    Input #1, em_285(i), Value_285(i)

  Next i

Close #1

Open "c:\SFStoolkit\ex_297.prn" For Input As #1

  For i = 1 To 27

    Input #1, em_297(i), Value_297(i)
```

```
Next i

Close #1

Open "c:\SFStoolkit\ex_309.prn" For Input As #1

  For i = 1 To 26

    Input #1, em_309(i), Value_309(i)

  Next i

Close #1

Open "c:\SFStoolkit\ex_321.prn" For Input As #1

  For i = 1 To 25

    Input #1, em_321(i), Value_321(i)

  Next i

Close #1

Open "c:\SFStoolkit\ex_333.prn" For Input As #1

  For i = 1 To 24

    Input #1, em_333(i), Value_333(i)

  Next i

Close #1

Open "c:\SFStoolkit\ex_345.prn" For Input As #1

  For i = 1 To 23

    Input #1, em_345(i), Value_345(i)

  Next i

Close #1

Open "c:\SFStoolkit\ex_357.prn" For Input As #1
```

```
For i = 1 To 22

    Input #1, em_357(i), Value_357(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_369.prn" For Input As #1

    For i = 1 To 21

        Input #1, em_369(i), Value_369(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_381.prn" For Input As #1

    For i = 1 To 20

        Input #1, em_381(i), Value_381(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_393.prn" For Input As #1

    For i = 1 To 19

        Input #1, em_393(i), Value_393(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_405.prn" For Input As #1

    For i = 1 To 18

        Input #1, em_405(i), Value_405(i)

    Next i
```

Close #1

Open "c:\SFStoolkit\ex_417.prn" For Input As #1

For i = 1 To 17

Input #1, em_417(i), Value_417(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_429.prn" For Input As #1

For i = 1 To 16

Input #1, em_429(i), Value_429(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_441.prn" For Input As #1

For i = 1 To 15

Input #1, em_441(i), Value_441(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_453.prn" For Input As #1

For i = 1 To 14

Input #1, em_453(i), Value_453(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_465.prn" For Input As #1

For i = 1 To 13

```
    Input #1, em_465(i), Value_465(i)
  Next i
Close #1
Open "c:\SFStoolkit\ex_477.prn" For Input As #1
  For i = 1 To 12
    Input #1, em_477(i), Value_477(i)
  Next i
Close #1
Open "c:\SFStoolkit\ex_489.prn" For Input As #1
  For i = 1 To 11
    Input #1, em_489(i), Value_489(i)
  Next i
Close #1
Open "c:\SFStoolkit\ex_501.prn" For Input As #1
  For i = 1 To 10
    Input #1, em_501(i), Value_501(i)
  Next i
Close #1
Open "c:\SFStoolkit\ex_513.prn" For Input As #1
  For i = 1 To 9
    Input #1, em_513(i), Value_513(i)
  Next i
Close #1
```


Open "c:\SFStoolkit\ex_525.prn" For Input As #1

For i = 1 To 8

Input #1, em_525(i), Value_525(i)

Next i

Close #1

'To Remove Scatters

For i = 1 To size225 - 1

If (Value_225(i + 1) - Value_225(i)) > 12 Then

Value_225(i + 1) = Value_225(i)

Else

Value_225(i) = Value_225(i)

End If

Next i

For i = 1 To size237 - 1

If (Value_237(i + 1) - Value_237(i)) > 12 Then

Value_237(i + 1) = Value_237(i)

Else

Value_237(i) = Value_237(i)

End If

Next i

```
For i = 1 To size249 - 1

    If (Value_249(i + 1) - Value_249(i)) > 12 Then

        Value_249(i + 1) = Value_249(i)

    Else

        Value_249(i) = Value_249(i)

    End If

Next i

For i = 1 To size261 - 1

    If (Value_261(i + 1) - Value_261(i)) > 12 Then

        Value_261(i + 1) = Value_261(i)

    Else

        Value_261(i) = Value_261(i)

    End If

Next i

For i = 1 To size273 - 1

    If (Value_273(i + 1) - Value_273(i)) > 12 Then

        Value_273(i + 1) = Value_273(i)

    Else

        Value_273(i) = Value_273(i)

    End If

Next i

For i = 1 To size285 - 1

    If (Value_285(i + 1) - Value_285(i)) > 12 Then
```

```
Value_285(i + 1) = Value_285(i)

Else

Value_285(i) = Value_285(i)

End If

Next i

For i = 1 To size297 - 1

If (Value_297(i + 1) - Value_297(i)) > 12 Then

Value_297(i + 1) = Value_297(i)

Else

Value_297(i) = Value_297(i)

End If

Next i

For i = 1 To size309 - 1

If (Value_309(i + 1) - Value_309(i)) > 12 Then

Value_309(i + 1) = Value_309(i)

Else

Value_309(i) = Value_309(i)

End If

Next i

For i = 1 To size321 - 1

If (Value_321(i + 1) - Value_321(i)) > 12 Then

Value_321(i + 1) = Value_321(i)

Else
```

```
Value_321(i) = Value_321(i)

End If

Next i

For i = 1 To size333 - 1

    If (Value_333(i + 1) - Value_333(i)) > 12 Then

        Value_333(i + 1) = Value_333(i)

    Else

        Value_333(i) = Value_333(i)

    End If

Next i

For i = 1 To size345 - 1

    If (Value_345(i + 1) - Value_345(i)) > 12 Then

        Value_345(i + 1) = Value_345(i)

    Else

        Value_345(i) = Value_345(i)

    End If

Next i

For i = 1 To size357 - 1

    If (Value_357(i + 1) - Value_357(i)) > 12 Then

        Value_357(i + 1) = Value_357(i)

    Else

        Value_357(i) = Value_357(i)

    End If
```

Next i

For i = 1 To size369 - 1

 If (Value_369(i + 1) - Value_369(i)) > 12 Then

 Value_369(i + 1) = Value_369(i)

 Else

 Value_369(i) = Value_369(i)

 End If

Next i

For i = 1 To size381 - 1

 If (Value_381(i + 1) - Value_381(i)) > 12 Then

 Value_381(i + 1) = Value_381(i)

 Else

 Value_381(i) = Value_381(i)

 End If

Next i

For i = 1 To size393 - 1

 If (Value_393(i + 1) - Value_393(i)) > 12 Then

 Value_393(i + 1) = Value_393(i)

 Else

 Value_393(i) = Value_393(i)

 End If

Next i

For i = 1 To size405 - 1

```
If (Value_405(i + 1) - Value_405(i)) > 12 Then
    Value_405(i + 1) = Value_405(i)
Else
    Value_405(i) = Value_405(i)
End If

Next i

For i = 1 To size417 - 1
    If (Value_417(i + 1) - Value_417(i)) > 12 Then
        Value_417(i + 1) = Value_417(i)
    Else
        Value_417(i) = Value_417(i)
    End If
End If

Next i

For i = 1 To size429 - 1
    If (Value_429(i + 1) - Value_429(i)) > 12 Then
        Value_429(i + 1) = Value_429(i)
    Else
        Value_429(i) = Value_429(i)
    End If
End If

Next i

For i = 1 To size441 - 1
    If (Value_441(i + 1) - Value_441(i)) > 12 Then
        Value_441(i + 1) = Value_441(i)
```

Else

Value_441(i) = Value_441(i)

End If

Next i

For i = 1 To size453 - 1

If (Value_453(i + 1) - Value_453(i)) > 12 Then

Value_453(i + 1) = Value_453(i)

Else

Value_453(i) = Value_453(i)

End If

Next i

For i = 1 To size465 - 1

If (Value_465(i + 1) - Value_465(i)) > 12 Then

Value_465(i + 1) = Value_465(i)

Else

Value_465(i) = Value_465(i)

End If

Next i

For i = 1 To size477 - 1

If (Value_477(i + 1) - Value_477(i)) > 12 Then

Value_477(i + 1) = Value_477(i)

Else

Value_477(i) = Value_477(i)

```
End If

Next i

For i = 1 To size489 - 1

    If (Value_489(i + 1) - Value_489(i)) > 12 Then

        Value_489(i + 1) = Value_489(i)

    Else

        Value_489(i) = Value_489(i)

    End If

Next i

For i = 1 To size501 - 1

    If (Value_501(i + 1) - Value_501(i)) > 12 Then

        Value_501(i + 1) = Value_501(i)

    Else

        Value_501(i) = Value_501(i)

    End If

Next i

For i = 1 To size513 - 1

    If (Value_513(i + 1) - Value_513(i)) > 12 Then

        Value_513(i + 1) = Value_513(i)

    Else

        Value_513(i) = Value_513(i)

    End If

Next i
```



```

For i = 1 To size525 - 1

    If (Value_525(i + 1) - Value_525(i)) > 12 Then

        Value_525(i + 1) = Value_525(i)

    Else

        Value_525(i) = Value_525(i)

    End If

Next i

'Computing the Spectral Strip Area

area = Value_225(9) * (327 - 321)

area225 = 0

For i = 1 To size225

    area225 = area225 + 12 * Value_225(i)

Next i

area225 = area225

slopeHFN = ((Abs(Value_225(6) - Value_225(4)) / 24) +
(Abs(Value_237(5) - Value_237(3)) / 24) + _
(Abs(Value_225(7) - Value_225(5)) / 24) + (Abs(Value_237(6) -
Value_237(4)) / 24)) / 4

frmFractionIDHPON.Show

Let frmFractionIDHPON.txtSlope.Text = slopeHFN

Let frmFractionIDHPON.txtArea.Text = area

Let frmFractionIDHPON.txtSF.Text = slopeHFN * area

End Sub

```

```

Private Sub cmdConcComputeHPIA_Click()

Dim slope, area, SF, concentration As Single

Let SF = Val(txtSF.Text)

frmToolkit.picResult.Cls

    frmToolkit.Show

    Select Case SF

        Case 3.78 To 5.38

            frmToolkit.picResult.Print "The concentration of this fraction is
0.1 ppm"

            frmToolkit.picResult.Print "You should proceed to record this
data"

        Case 4.24 To 5.74

            frmToolkit.picResult.Print "The concentration of this fraction is
0.2 ppm"

            frmToolkit.picResult.Print "You should proceed to record this
data"

        Case 5.64 To 7.64

            frmToolkit.picResult.Print "The concentration of this fraction is
0.4 ppm"

            frmToolkit.picResult.Print "You should proceed to record this
data"

        Case 37.53 To 50.76

            frmToolkit.picResult.Print "The concentration of this fraction is

```

```

0.6 ppm"

frmToolkit.picResult.Print "You should proceed to record this
data"

Case Else

conc = 0.2 * SF + 1.08

frmToolkit.picResult.Print "The concentration of this fraction is
", conc

frmToolkit.picResult.Print "You should proceed to record this
data =====>>>>"

End Select

End Sub

Private Sub cmdDBPCompute_Click()

frmYourResponse.Show

End Sub

Private Sub cmdConcComputeHPiB_Click()

Dim slope, area, SF, concentration As Single

Let SF = Val(txtSF.Text)

frmToolkit.picResult.Cls

frmToolkit.Show

Select Case SF

Case 2.48 To 3.35

frmToolkit.picResult.Print "The concentration of this fraction is
0.1 ppm"

```

```
frmToolkit.picResult.Print "You should proceed to record this  
data"
```

Case 2.05 To 2.77

```
frmToolkit.picResult.Print "The concentration of this fraction is  
0.2 ppm"
```

```
frmToolkit.picResult.Print "You should proceed to record this  
data"
```

Case 2.73 To 3.7

```
frmToolkit.picResult.Print "The concentration of this fraction is  
0.4 ppm"
```

```
frmToolkit.picResult.Print "You should proceed to record this  
data"
```

Case 3.44 To 4.66

```
frmToolkit.picResult.Print "The concentration of this fraction is  
0.6 ppm"
```

```
frmToolkit.picResult.Print "You should proceed to record this  
data"
```

Case 4.1 To 5.52

```
frmToolkit.picResult.Print "The concentration of this fraction is  
0.8 ppm"
```

```
frmToolkit.picResult.Print "You should proceed to record this  
data"
```

Case 3.99 To 5.39

```

frmToolkit.picResult.Print "The concentration of this fraction is
1 ppm"

frmToolkit.picResult.Print "You should proceed to record this
data"

Case Else

conc = 0.05 * SF + 0.11

frmToolkit.picResult.Print "The concentration of this fraction is
", conc

frmToolkit.picResult.Print "You should proceed to record this
data =====>>>>"

End Select

End Sub

```

```

Private Sub cmdDBPCompute_Click()

frmYourResponse.Show

End Sub

Private Sub cmdConcComputeHPIN_Click()

Dim slope, area, SF, concentration As Single

Let SF = Val(txtSF.Text)

frmToolkit.picResult.Cls

frmToolkit.Show

Select Case SF

Case 0.51 To 0.7

```

```
frmToolkit.picResult.Print "The concentration of this fraction is  
0.1 ppm"
```

```
frmToolkit.picResult.Print "You should proceed to record this  
data"
```

Case 0.65 To 0.87

```
frmToolkit.picResult.Print "The concentration of this fraction is  
0.2 ppm"
```

```
frmToolkit.picResult.Print "You should proceed to record this  
data"
```

Case 1.62 To 2.19

```
frmToolkit.picResult.Print "The concentration of this fraction is  
0.4 ppm"
```

```
frmToolkit.picResult.Print "You should proceed to record this  
data"
```

Case 3.49 To 4.72

```
frmToolkit.picResult.Print "The concentration of this fraction is  
0.8 ppm"
```

Case 3.69 To 5

```
frmToolkit.picResult.Print "The concentration of this fraction is  
1 ppm"
```

```
frmToolkit.picResult.Print "You should proceed to record this  
data"
```

Case Else

```

conc = 17 * SF + 0.02

frmToolkit.picResult.Print "The concentration of this fraction is

", conc

frmToolkit.picResult.Print "You should proceed to record this
data =====>>>>"

End Select

End Sub

Private Sub cmdDBPCompute_Click()

frmYourResponse.Show

End Sub

Private Sub cmdConcComputeHPOA_Click()

Dim slope, area, SF, concentration As Single

Let SF = Val(txtSF.Text)

frmToolkit.picResult.Cls

frmToolkit.Show

Select Case SF

Case 0.62 To 0.83

frmToolkit.picResult.Print "The concentration of this fraction is

0.1 ppm"

frmToolkit.picResult.Print "You should proceed to record this
data =====>>>>"

Case 1.73 To 2.33

```

```
frmToolkit.picResult.Print "The concentration of this fraction is  
0.2 ppm"
```

```
frmToolkit.picResult.Print "You should proceed to record this  
data =====>>>>"
```

Case 4.25 To 5.75

```
frmToolkit.picResult.Print "The concentration of this fraction is  
0.4 ppm"
```

```
frmToolkit.picResult.Print "You should proceed to record this  
data =====>>>>"
```

Case 8.33 To 11.27

```
frmToolkit.picResult.Print "The concentration of this fraction is  
0.6 ppm"
```

```
frmToolkit.picResult.Print "You should proceed to record this  
data =====>>>>"
```

Case 13.1 To 17.7

```
frmToolkit.picResult.Print "The concentration of this fraction is  
0.8 ppm"
```

```
frmToolkit.picResult.Print "You should proceed to record this  
data =====>>>>"
```

Case 19.1 To 24.48

```
frmToolkit.picResult.Print "The concentration of this fraction is  
1 ppm"
```

```
frmToolkit.picResult.Print "You should proceed to record this
```



```
data =====>>>>"
```

```
Case Else
```

```
conc = 0.03 * SF + 0.2
```

```
frmToolkit.picResult.Print "The concentration of this fraction is
```

```
", conc
```

```
frmToolkit.picResult.Print "You should proceed to record this
```

```
data =====>>>>"
```

```
End Select
```

```
End Sub
```

```
Private Sub cmdDBPCompute_Click()
```

```
frmYourResponse.Show
```

```
End Sub
```

```
Private Sub cmdConcComputeHPOB_Click()
```

```
Dim slope, area, SF, concentration As Single
```

```
Let SF = Val(txtSF.Text)
```

```
frmToolkit.picResult.Cls
```

```
frmToolkit.Show
```

```
Select Case SF
```

```
Case 2.52 To 3.41
```

```
frmToolkit.picResult.Print "The concentration of this fraction is
```

```
0.1 ppm"
```

```
frmToolkit.picResult.Print "You should proceed to record this
```

```
data =====>>>>"
```

Case 5.78 To 7.82

```
frmToolkit.picResult.Print "The concentration of this fraction is  
0.2 ppm"
```

```
frmToolkit.picResult.Print "You should proceed to record this  
data =====>>>>"
```

Case 20 To 27.1

```
frmToolkit.picResult.Print "The concentration of this fraction is  
0.4 ppm"
```

```
frmToolkit.picResult.Print "You should proceed to record this  
data =====>>>>"
```

Case 18.96 To 25.65

```
frmToolkit.picResult.Print "The concentration of this fraction is  
0.6 ppm"
```

```
frmToolkit.picResult.Print "You should proceed to record this  
data =====>>>>"
```

Case Else

```
conc = 0.26 * SF + 0.02
```

```
frmToolkit.picResult.Print "The concentration of this fraction is  
"; conc
```

```
frmToolkit.picResult.Print "You should proceed to record this  
data =====>>>>"
```

End Select

End Sub

```

Private Sub cmdDBPCompute_Click()

frmYourResponse.Show

End Sub

Private Sub cmdConcComputeHPON_Click()

Dim slope, area, SF, concentration As Single

Let SF = Val(txtSF.Text)

frmToolkit.picResult.Cls

    frmToolkit.Show

    Select Case SF

        Case 11.2 To 15.15

            frmToolkit.picResult.Print "The concentration of this fraction is

0.1 ppm"

            frmToolkit.picResult.Print "You should proceed to record this

data"

        Case 21.2 To 28.65

            frmToolkit.picResult.Print "The concentration of this fraction is

0.2 ppm"

            frmToolkit.picResult.Print "You should proceed to record this

data"

        Case 50.85 To 60.8

            frmToolkit.picResult.Print "The concentration of this fraction is

0.4 ppm"

```

```
frmToolkit.picResult.Print "You should proceed to record this
data"
```

```
Case 77.83 To 105.3
```

```
frmToolkit.picResult.Print "The concentration of this fraction is
0.6 ppm"
```

```
frmToolkit.picResult.Print "You should proceed to record this
data"
```

```
Case 166.1 To 224.7
```

```
frmToolkit.picResult.Print "The concentration of this fraction is
0.8 ppm"
```

```
frmToolkit.picResult.Print "You should proceed to record this
data"
```

```
Case 281.5 To 380.85
```

```
frmToolkit.picResult.Print "The concentration of this fraction is
1 ppm"
```

```
frmToolkit.picResult.Print "You should proceed to record this
data"
```

```
Case Else
```

```
conc = 0.15 * SF + 0.3
```

```
frmToolkit.picResult.Print "The concentration of this fraction is
", conc
```

```
frmToolkit.picResult.Print "You should proceed to record this
data =====>>>>"
```

End Select

End Sub

Private Sub cmdDBPCompute_Click()

frmYourResponse.Show

End Sub

Private Sub cmdCdrive_Click()

frmToolkit.picResult.Cls

Dim ex_225(1 To 33, 1 To 2) As Single

Dim ex_237(1 To 32, 1 To 2) As Single

Dim ex_249(1 To 31, 1 To 2) As Single

Dim ex_261(1 To 30, 1 To 2) As Single

Dim ex_273(1 To 29, 1 To 2) As Single

Dim ex_285(1 To 28, 1 To 2) As Single

Dim ex_297(1 To 27, 1 To 2) As Single

Dim ex_309(1 To 26, 1 To 2) As Single

Dim ex_321(1 To 25, 1 To 2) As Single

Dim ex_333(1 To 24, 1 To 2) As Single

Dim ex_345(1 To 23, 1 To 2) As Single

Dim ex_357(1 To 22, 1 To 2) As Single

Dim ex_369(1 To 21, 1 To 2) As Single

Dim ex_381(1 To 20, 1 To 2) As Single

Dim ex_393(1 To 19, 1 To 2) As Single

Dim ex_405(1 To 18, 1 To 2) As Single

```

Dim ex_417(1 To 17, 1 To 2) As Single
Dim ex_429(1 To 16, 1 To 2) As Single
Dim ex_441(1 To 15, 1 To 2) As Single
Dim ex_453(1 To 14, 1 To 2) As Single
Dim ex_465(1 To 13, 1 To 2) As Single
Dim ex_477(1 To 12, 1 To 2) As Single
Dim ex_489(1 To 11, 1 To 2) As Single
Dim ex_501(1 To 10, 1 To 2) As Single
Dim ex_513(1 To 9, 1 To 2) As Single
Dim ex_525(1 To 8, 1 To 2) As Single
Dim em_225(1 To 33), em_237(1 To 32), em_249(1 To 31),
em_261(1 To 30), _
em_273(1 To 29), em_285(1 To 28), em_297(1 To 27),
em_309(1 To 26), _
em_321(1 To 25), em_333(1 To 24), em_345(1 To 23),
em_357(1 To 22), _
em_369(1 To 21), em_381(1 To 20), em_393(1 To 19),
em_405(1 To 18), _
em_417(1 To 17), em_429(1 To 16), em_441(1 To 15),
em_453(1 To 14), _
em_465(1 To 13), em_477(1 To 12), em_489(1 To 11),
em_501(1 To 10), _
em_513(1 To 9), em_525(1 To 8) As Integer

```

Dim Value_225(1 To 33), Value_237(1 To 32), Value_249(1 To
 31), Value_261(1 To 30), _
 Value_273(1 To 29), Value_285(1 To 28), Value_297(1 To 27),
 Value_309(1 To 26), _
 Value_321(1 To 25), Value_333(1 To 24), Value_345(1 To 23),
 Value_357(1 To 22), _
 Value_369(1 To 21), Value_381(1 To 20), Value_393(1 To 19),
 Value_405(1 To 18), _
 Value_417(1 To 17), Value_429(1 To 16), Value_441(1 To 15),
 Value_453(1 To 14), _
 Value_465(1 To 13), Value_477(1 To 12), Value_489(1 To 11),
 Value_501(1 To 10), _
 Value_513(1 To 9), Value_525(1 To 8), slopeHPOB As Single
 Dim size225, size237, size249, size261, size273, size285,
 size297, _
 size309, size321, size333, size345, size357, size369, size381, _
 size393, size405, size417, size429, size441, size453, size465, _
 size477, size489, size501, size513, size525 As Integer
 size225 = 33
 size237 = 32
 size249 = 31
 size261 = 30
 size273 = 29

size285 = 28

size297 = 27

size309 = 26

size321 = 25

size333 = 24

size345 = 23

size357 = 22

size369 = 21

size381 = 20

size393 = 19

size405 = 18

size417 = 17

size429 = 16

size441 = 15

size453 = 14

size465 = 13

size477 = 12

size489 = 11

size501 = 10

size513 = 9

size525 = 8

Open "c:\SFStoolkit\ex_225.prm" For Input As #1


```
For i = 1 To 33
    Input #1, em_225(i), Value_225(i)
Next i
Close #1
Open "c:\SFStoolkit\ex_237.prm" For Input As #1
    For i = 1 To 32
        Input #1, em_237(i), Value_237(i)
    Next i
Close #1
Open "c:\SFStoolkit\ex_249.prm" For Input As #1
    For i = 1 To 31
        Input #1, em_249(i), Value_249(i)
    Next i
Close #1
Open "c:\SFStoolkit\ex_261.prm" For Input As #1
    For i = 1 To 30
        Input #1, em_261(i), Value_261(i)
    Next i
Close #1
Open "c:\SFStoolkit\ex_273.prm" For Input As #1
    For i = 1 To 29
        Input #1, em_273(i), Value_273(i)
    Next i
```

Close #1

Open "c:\SFStoolkit\ex_285.prn" For Input As #1

For i = 1 To 28

Input #1, em_285(i), Value_285(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_297.prn" For Input As #1

For i = 1 To 27

Input #1, em_297(i), Value_297(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_309.prn" For Input As #1

For i = 1 To 26

Input #1, em_309(i), Value_309(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_321.prn" For Input As #1

For i = 1 To 25

Input #1, em_321(i), Value_321(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_333.prn" For Input As #1

```
For i = 1 To 24

    Input #1, em_333(i), Value_333(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_345.prn" For Input As #1

    For i = 1 To 23

        Input #1, em_345(i), Value_345(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_357.prn" For Input As #1

    For i = 1 To 22

        Input #1, em_357(i), Value_357(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_369.prn" For Input As #1

    For i = 1 To 21

        Input #1, em_369(i), Value_369(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_381.prn" For Input As #1

    For i = 1 To 20

        Input #1, em_381(i), Value_381(i)

    Next i
```

Close #1

Open "c:\SFStoolkit\ex_393.prn" For Input As #1

For i = 1 To 19

Input #1, em_393(i), Value_393(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_405.prn" For Input As #1

For i = 1 To 18

Input #1, em_405(i), Value_405(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_417.prn" For Input As #1

For i = 1 To 17

Input #1, em_417(i), Value_417(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_429.prn" For Input As #1

For i = 1 To 16

Input #1, em_429(i), Value_429(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_441.prn" For Input As #1

```
For i = 1 To 15

    Input #1, em_441(i), Value_441(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_453.prn" For Input As #1

    For i = 1 To 14

        Input #1, em_453(i), Value_453(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_465.prn" For Input As #1

    For i = 1 To 13

        Input #1, em_465(i), Value_465(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_477.prn" For Input As #1

    For i = 1 To 12

        Input #1, em_477(i), Value_477(i)

    Next i

Close #1

Open "c:\SFStoolkit\ex_489.prn" For Input As #1

    For i = 1 To 11

        Input #1, em_489(i), Value_489(i)

    Next i
```

Close #1

Open "c:\SFStoolkit\ex_501.prn" For Input As #1

For i = 1 To 10

Input #1, em_501(i), Value_501(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_513.prn" For Input As #1

For i = 1 To 9

Input #1, em_513(i), Value_513(i)

Next i

Close #1

Open "c:\SFStoolkit\ex_525.prn" For Input As #1

For i = 1 To 8

Input #1, em_525(i), Value_525(i)

Next i

Close #1

'=====

'To Remove Scatters

For i = 1 To size225 - 1

If (Value_225(i + 1) - Value_225(i)) > 12 Then

Value_225(i + 1) = Value_225(i)

Else

```
Value_225(i) = Value_225(i)

End If

Next i

For i = 1 To size237 - 1

    If (Value_237(i + 1) - Value_237(i)) > 12 Then

        Value_237(i + 1) = Value_237(i)

    Else

        Value_237(i) = Value_237(i)

    End If

Next i

For i = 1 To size249 - 1

    If (Value_249(i + 1) - Value_249(i)) > 12 Then

        Value_249(i + 1) = Value_249(i)

    Else

        Value_249(i) = Value_249(i)

    End If

Next i

For i = 1 To size261 - 1

    If (Value_261(i + 1) - Value_261(i)) > 12 Then

        Value_261(i + 1) = Value_261(i)

    Else

        Value_261(i) = Value_261(i)

    End If
```

Next i

For i = 1 To size273 - 1

 If (Value_273(i + 1) - Value_273(i)) > 12 Then

 Value_273(i + 1) = Value_273(i)

 Else

 Value_273(i) = Value_273(i)

 End If

Next i

For i = 1 To size285 - 1

 If (Value_285(i + 1) - Value_285(i)) > 12 Then

 Value_285(i + 1) = Value_285(i)

 Else

 Value_285(i) = Value_285(i)

 End If

Next i

For i = 1 To size297 - 1

 If (Value_297(i + 1) - Value_297(i)) > 12 Then

 Value_297(i + 1) = Value_297(i)

 Else

 Value_297(i) = Value_297(i)

 End If

Next i


```
For i = 1 To size309 - 1

    If (Value_309(i + 1) - Value_309(i)) > 12 Then

        Value_309(i + 1) = Value_309(i)

    Else

        Value_309(i) = Value_309(i)

    End If

Next i

For i = 1 To size321 - 1

    If (Value_321(i + 1) - Value_321(i)) > 12 Then

        Value_321(i + 1) = Value_321(i)

    Else

        Value_321(i) = Value_321(i)

    End If

Next i

For i = 1 To size333 - 1

    If (Value_333(i + 1) - Value_333(i)) > 12 Then

        Value_333(i + 1) = Value_333(i)

    Else

        Value_333(i) = Value_333(i)

    End If

Next i

For i = 1 To size345 - 1

    If (Value_345(i + 1) - Value_345(i)) > 12 Then
```

```
Value_345(i + 1) = Value_345(i)

Else

Value_345(i) = Value_345(i)

End If

Next i

For i = 1 To size357 - 1

If (Value_357(i + 1) - Value_357(i)) > 12 Then

Value_357(i + 1) = Value_357(i)

Else

Value_357(i) = Value_357(i)

End If

Next i

For i = 1 To size369 - 1

If (Value_369(i + 1) - Value_369(i)) > 12 Then

Value_369(i + 1) = Value_369(i)

Else

Value_369(i) = Value_369(i)

End If

Next i

For i = 1 To size381 - 1

If (Value_381(i + 1) - Value_381(i)) > 12 Then

Value_381(i + 1) = Value_381(i)

Else
```

```
Value_381(i) = Value_381(i)

End If

Next i

For i = 1 To size393 - 1

    If (Value_393(i + 1) - Value_393(i)) > 12 Then

        Value_393(i + 1) = Value_393(i)

    Else

        Value_393(i) = Value_393(i)

    End If

Next i

For i = 1 To size405 - 1

    If (Value_405(i + 1) - Value_405(i)) > 12 Then

        Value_405(i + 1) = Value_405(i)

    Else

        Value_405(i) = Value_405(i)

    End If

Next i

For i = 1 To size417 - 1

    If (Value_417(i + 1) - Value_417(i)) > 12 Then

        Value_417(i + 1) = Value_417(i)

    Else

        Value_417(i) = Value_417(i)

    End If
```

Next i

For i = 1 To size429 - 1

 If (Value_429(i + 1) - Value_429(i)) > 12 Then

 Value_429(i + 1) = Value_429(i)

 Else

 Value_429(i) = Value_429(i)

 End If

Next i

For i = 1 To size441 - 1

 If (Value_441(i + 1) - Value_441(i)) > 12 Then

 Value_441(i + 1) = Value_441(i)

 Else

 Value_441(i) = Value_441(i)

 End If

Next i

For i = 1 To size453 - 1

 If (Value_453(i + 1) - Value_453(i)) > 12 Then

 Value_453(i + 1) = Value_453(i)

 Else

 Value_453(i) = Value_453(i)

 End If

Next i

```
For i = 1 To size465 - 1

    If (Value_465(i + 1) - Value_465(i)) > 12 Then

        Value_465(i + 1) = Value_465(i)

    Else

        Value_465(i) = Value_465(i)

    End If

Next i

For i = 1 To size477 - 1

    If (Value_477(i + 1) - Value_477(i)) > 12 Then

        Value_477(i + 1) = Value_477(i)

    Else

        Value_477(i) = Value_477(i)

    End If

Next i

For i = 1 To size489 - 1

    If (Value_489(i + 1) - Value_489(i)) > 12 Then

        Value_489(i + 1) = Value_489(i)

    Else

        Value_489(i) = Value_489(i)

    End If

Next i

For i = 1 To size501 - 1

    If (Value_501(i + 1) - Value_501(i)) > 12 Then
```

```

    Value_501(i + 1) = Value_501(i)

Else

    Value_501(i) = Value_501(i)

End If

Next i

For i = 1 To size513 - 1

    If (Value_513(i + 1) - Value_513(i)) > 12 Then

        Value_513(i + 1) = Value_513(i)

    Else

        Value_513(i) = Value_513(i)

    End If

Next i

For i = 1 To size525 - 1

    If (Value_525(i + 1) - Value_525(i)) > 12 Then

        Value_525(i + 1) = Value_525(i)

    Else

        Value_525(i) = Value_525(i)

    End If

Next i

'For i = 225 To 525 Step 12

    frmToolkit.Show

    frmToolkit.picResult.Print "Data File Has Been Loaded"

    frmToolkit.picResult.Print "Please Select The Fractions Below

```

```

to Operate on (One At a Time)"

' frmToolkit.picResult.Print "Spectral Data for excitation ="; i;
" is";

' For j = 1 To size225

'     frmToolkit.picResult.Print Tab(50); em_225(j); Tab(60);
Value_225(j)

'     If j = size225 Then

'         frmToolkit.picResult.Print ""

'     Else

'     End If

' Next j

'Next i

End Sub

Private Sub cmdAdrive_Click()

frmToolkit.picResult.Cls

Dim ex_225(1 To 33, 1 To 2) As Single

    Dim ex_237(1 To 32, 1 To 2) As Single

    Dim ex_249(1 To 31, 1 To 2) As Single

    Dim ex_261(1 To 30, 1 To 2) As Single

    Dim ex_273(1 To 29, 1 To 2) As Single

    Dim ex_285(1 To 28, 1 To 2) As Single

    Dim ex_297(1 To 27, 1 To 2) As Single

    Dim ex_309(1 To 26, 1 To 2) As Single

```

Dim ex_321(1 To 25, 1 To 2) As Single
 Dim ex_333(1 To 24, 1 To 2) As Single
 Dim ex_345(1 To 23, 1 To 2) As Single
 Dim ex_357(1 To 22, 1 To 2) As Single
 Dim ex_369(1 To 21, 1 To 2) As Single
 Dim ex_381(1 To 20, 1 To 2) As Single
 Dim ex_393(1 To 19, 1 To 2) As Single
 Dim ex_405(1 To 18, 1 To 2) As Single
 Dim ex_417(1 To 17, 1 To 2) As Single
 Dim ex_429(1 To 16, 1 To 2) As Single
 Dim ex_441(1 To 15, 1 To 2) As Single
 Dim ex_453(1 To 14, 1 To 2) As Single
 Dim ex_465(1 To 13, 1 To 2) As Single
 Dim ex_477(1 To 12, 1 To 2) As Single
 Dim ex_489(1 To 11, 1 To 2) As Single
 Dim ex_501(1 To 10, 1 To 2) As Single
 Dim ex_513(1 To 9, 1 To 2) As Single
 Dim ex_525(1 To 8, 1 To 2) As Single
 Dim em_225(1 To 33), em_237(1 To 32), em_249(1 To 31),
 em_261(1 To 30), _
 em_273(1 To 29), em_285(1 To 28), em_297(1 To 27),
 em_309(1 To 26), _
 em_321(1 To 25), em_333(1 To 24), em_345(1 To 23),


```

em_357(1 To 22), _
em_369(1 To 21), em_381(1 To 20), em_393(1 To 19),
em_405(1 To 18), _
em_417(1 To 17), em_429(1 To 16), em_441(1 To 15),
em_453(1 To 14), _
em_465(1 To 13), em_477(1 To 12), em_489(1 To 11),
em_501(1 To 10), _
em_513(1 To 9), em_525(1 To 8) As Integer
Dim Value_225(1 To 33), Value_237(1 To 32), Value_249(1 To
31), Value_261(1 To 30), _
Value_273(1 To 29), Value_285(1 To 28), Value_297(1 To 27),
Value_309(1 To 26), _
Value_321(1 To 25), Value_333(1 To 24), Value_345(1 To 23),
Value_357(1 To 22), _
Value_369(1 To 21), Value_381(1 To 20), Value_393(1 To 19),
Value_405(1 To 18), _
Value_417(1 To 17), Value_429(1 To 16), Value_441(1 To 15),
Value_453(1 To 14), _
Value_465(1 To 13), Value_477(1 To 12), Value_489(1 To 11),
Value_501(1 To 10), _
Value_513(1 To 9), Value_525(1 To 8), slopeHPOB As Single
Dim size225, size237, size249, size261, size273, size285,
size297, _

```

size309, size321, size333, size345, size357, size369, size381, _
size393, size405, size417, size429, size441, size453, size465, _
size477, size489, size501, size513, size525 As Integer

size225 = 33

size237 = 32

size249 = 31

size261 = 30

size273 = 29

size285 = 28

size297 = 27

size309 = 26

size321 = 25

size333 = 24

size345 = 23

size357 = 22

size369 = 21

size381 = 20

size393 = 19

size405 = 18

size417 = 17

size429 = 16

size441 = 15

size453 = 14

```
size465 = 13

size477 = 12

size489 = 11

size501 = 10

size513 = 9

size525 = 8

Open "a:\ex_225.prn" For Input As #1

For i = 1 To 33

Input #1, em_225(i), Value_225(i)

Next i

Close #1

Open "a:\ex_237.prn" For Input As #1

For i = 1 To 32

Input #1, em_237(i), Value_237(i)

Next i

Close #1

Open "a:\ex_249.prn" For Input As #1

For i = 1 To 31

Input #1, em_249(i), Value_249(i)

Next i

Close #1

Open "a:\ex_261.prn" For Input As #1

For i = 1 To 30
```

```
    Input #1, em_261(i), Value_261(i)
  Next i
Close #1

Open "a:\ex_273.prn" For Input As #1
  For i = 1 To 29
    Input #1, em_273(i), Value_273(i)
  Next i
Close #1

Open "a:\ex_285.prn" For Input As #1
  For i = 1 To 28
    Input #1, em_285(i), Value_285(i)
  Next i
Close #1

Open "a:\ex_297.prn" For Input As #1
  For i = 1 To 27
    Input #1, em_297(i), Value_297(i)
  Next i
Close #1

Open "a:\ex_309.prn" For Input As #1
  For i = 1 To 26
    Input #1, em_309(i), Value_309(i)
  Next i
Close #1
```

```
Open "a:\ex_321.prm" For Input As #1
```

```
For i = 1 To 25
```

```
Input #1, em_321(i), Value_321(i)
```

```
Next i
```

```
Close #1
```

```
Open "a:\ex_333.prm" For Input As #1
```

```
For i = 1 To 24
```

```
Input #1, em_333(i), Value_333(i)
```

```
Next i
```

```
Close #1
```

```
Open "a:\ex_345.prm" For Input As #1
```

```
For i = 1 To 23
```

```
Input #1, em_345(i), Value_345(i)
```

```
Next i
```

```
Close #1
```

```
Open "a:\ex_357.prm" For Input As #1
```

```
For i = 1 To 22
```

```
Input #1, em_357(i), Value_357(i)
```

```
Next i
```

```
Close #1
```

```
Open "a:\ex_369.prm" For Input As #1
```

```
For i = 1 To 21
```

```
Input #1, em_369(i), Value_369(i)
```

```
Next i

Close #1

Open "a:\ex_381.prn" For Input As #1

  For i = 1 To 20

    Input #1, em_381(i), Value_381(i)

  Next i

Close #1

Open "a:\ex_393.prn" For Input As #1

  For i = 1 To 19

    Input #1, em_393(i), Value_393(i)

  Next i

Close #1

Open "a:\ex_405.prn" For Input As #1

  For i = 1 To 18

    Input #1, em_405(i), Value_405(i)

  Next i

Close #1

Open "a:\ex_417.prn" For Input As #1

  For i = 1 To 17

    Input #1, em_417(i), Value_417(i)

  Next i

Close #1

Open "a:\ex_429.prn" For Input As #1
```

```
For i = 1 To 16

    Input #1, em_429(i), Value_429(i)

Next i

Close #1

Open "a:\ex_441.prm" For Input As #1

    For i = 1 To 15

        Input #1, em_441(i), Value_441(i)

    Next i

Close #1

Open "a:\ex_453.prm" For Input As #1

    For i = 1 To 14

        Input #1, em_453(i), Value_453(i)

    Next i

Close #1

Open "a:\ex_465.prm" For Input As #1

    For i = 1 To 13

        Input #1, em_465(i), Value_465(i)

    Next i

Close #1

Open "a:\ex_477.prm" For Input As #1

    For i = 1 To 12

        Input #1, em_477(i), Value_477(i)

    Next i
```

Close #1

Open "a:\ex_489.prn" For Input As #1

For i = 1 To 11

Input #1, em_489(i), Value_489(i)

Next i

Close #1

Open "a:\ex_501.prn" For Input As #1

For i = 1 To 10

Input #1, em_501(i), Value_501(i)

Next i

Close #1

Open "a:\ex_513.prn" For Input As #1

For i = 1 To 9

Input #1, em_513(i), Value_513(i)

Next i

Close #1

Open "a:\ex_525.prn" For Input As #1

For i = 1 To 8

Input #1, em_525(i), Value_525(i)

Next i

Close #1

'To Remove Scatters


```
For i = 1 To size225 - 1

    If (Value_225(i + 1) - Value_225(i)) > 12 Then

        Value_225(i + 1) = Value_225(i)

    Else

        Value_225(i) = Value_225(i)

    End If

Next i

For i = 1 To size237 - 1

    If (Value_237(i + 1) - Value_237(i)) > 12 Then

        Value_237(i + 1) = Value_237(i)

    Else

        Value_237(i) = Value_237(i)

    End If

Next i

For i = 1 To size249 - 1

    If (Value_249(i + 1) - Value_249(i)) > 12 Then

        Value_249(i + 1) = Value_249(i)

    Else

        Value_249(i) = Value_249(i)

    End If

Next i

For i = 1 To size261 - 1

    If (Value_261(i + 1) - Value_261(i)) > 12 Then
```

Value_261(i + 1) = Value_261(i)

Else

Value_261(i) = Value_261(i)

End If

Next i

For i = 1 To size273 - 1

If (Value_273(i + 1) - Value_273(i)) > 12 Then

Value_273(i + 1) = Value_273(i)

Else

Value_273(i) = Value_273(i)

End If

Next i

For i = 1 To size285 - 1

If (Value_285(i + 1) - Value_285(i)) > 12 Then

Value_285(i + 1) = Value_285(i)

Else

Value_285(i) = Value_285(i)

End If

Next i

For i = 1 To size297 - 1

If (Value_297(i + 1) - Value_297(i)) > 12 Then

Value_297(i + 1) = Value_297(i)

Else

Value_297(i) = Value_297(i)

End If

Next i

For i = 1 To size309 - 1

If (Value_309(i + 1) - Value_309(i)) > 12 Then

Value_309(i + 1) = Value_309(i)

Else

Value_309(i) = Value_309(i)

End If

Next i

For i = 1 To size321 - 1

If (Value_321(i + 1) - Value_321(i)) > 12 Then

Value_321(i + 1) = Value_321(i)

Else

Value_321(i) = Value_321(i)

End If

Next i

For i = 1 To size333 - 1

If (Value_333(i + 1) - Value_333(i)) > 12 Then

Value_333(i + 1) = Value_333(i)

Else

Value_333(i) = Value_333(i)

End If

Next i

For i = 1 To size345 - 1

 If (Value_345(i + 1) - Value_345(i)) > 12 Then

 Value_345(i + 1) = Value_345(i)

 Else

 Value_345(i) = Value_345(i)

 End If

Next i

For i = 1 To size357 - 1

 If (Value_357(i + 1) - Value_357(i)) > 12 Then

 Value_357(i + 1) = Value_357(i)

 Else

 Value_357(i) = Value_357(i)

 End If

Next i

For i = 1 To size369 - 1

 If (Value_369(i + 1) - Value_369(i)) > 12 Then

 Value_369(i + 1) = Value_369(i)

 Else

 Value_369(i) = Value_369(i)

 End If

Next i

For i = 1 To size381 - 1

```

If (Value_381(i + 1) - Value_381(i)) > 12 Then
    Value_381(i + 1) = Value_381(i)
Else
    Value_381(i) = Value_381(i)
End If
Next i

For i = 1 To size393 - 1
    If (Value_393(i + 1) - Value_393(i)) > 12 Then
        Value_393(i + 1) = Value_393(i)
    Else
        Value_393(i) = Value_393(i)
    End If
Next i

For i = 1 To size405 - 1
    If (Value_405(i + 1) - Value_405(i)) > 12 Then
        Value_405(i + 1) = Value_405(i)
    Else
        Value_405(i) = Value_405(i)
    End If
Next i

For i = 1 To size417 - 1
    If (Value_417(i + 1) - Value_417(i)) > 12 Then
        Value_417(i + 1) = Value_417(i)

```

```
Else

    Value_417(i) = Value_417(i)

End If

Next i

For i = 1 To size429 - 1

    If (Value_429(i + 1) - Value_429(i)) > 12 Then

        Value_429(i + 1) = Value_429(i)

    Else

        Value_429(i) = Value_429(i)

    End If

Next i

For i = 1 To size441 - 1

    If (Value_441(i + 1) - Value_441(i)) > 12 Then

        Value_441(i + 1) = Value_441(i)

    Else

        Value_441(i) = Value_441(i)

    End If

Next i

For i = 1 To size453 - 1

    If (Value_453(i + 1) - Value_453(i)) > 12 Then

        Value_453(i + 1) = Value_453(i)

    Else

        Value_453(i) = Value_453(i)
```

```
End If

Next i

For i = 1 To size465 - 1

    If (Value_465(i + 1) - Value_465(i)) > 12 Then

        Value_465(i + 1) = Value_465(i)

    Else

        Value_465(i) = Value_465(i)

    End If

Next i

For i = 1 To size477 - 1

    If (Value_477(i + 1) - Value_477(i)) > 12 Then

        Value_477(i + 1) = Value_477(i)

    Else

        Value_477(i) = Value_477(i)

    End If

Next i

For i = 1 To size489 - 1

    If (Value_489(i + 1) - Value_489(i)) > 12 Then

        Value_489(i + 1) = Value_489(i)

    Else

        Value_489(i) = Value_489(i)

    End If

Next i
```

```

For i = 1 To size501 - 1

    If (Value_501(i + 1) - Value_501(i)) > 12 Then

        Value_501(i + 1) = Value_501(i)

    Else

        Value_501(i) = Value_501(i)

    End If

Next i

For i = 1 To size513 - 1

    If (Value_513(i + 1) - Value_513(i)) > 12 Then

        Value_513(i + 1) = Value_513(i)

    Else

        Value_513(i) = Value_513(i)

    End If

Next i

For i = 1 To size525 - 1

    If (Value_525(i + 1) - Value_525(i)) > 12 Then

        Value_525(i + 1) = Value_525(i)

    Else

        Value_525(i) = Value_525(i)

    End If

Next i

For i = 225 To 525 Step 12

    frmToolkit.Show

```



```

frmToolkit.picResult.Print "Data File Has Been Loaded"

frmToolkit.picResult.Print "Please Select The Fractions Below
to Operate on (One At a Time)"

' frmToolkit.picResult.Print "Spectral Data for excitation ="; i; "
is";

' For j = 1 To size225

'     frmToolkit.picResult.Print Tab(50); em_225(j); Tab(60);
Value_225(j)

'     If j = size225 Then

'         frmToolkit.picResult.Print ""

'     Else

'         End If

'     Next j

Next i

End Sub

Private Sub cmdBackascreen_Click()

frmToolkit.Show

End Sub

Private Sub cmdComputeTHMFP_Click()

Dim DOC As Single, conc_hopb As Single, conc_hpoa As Single,
conc_hpon As Single

Dim conc_hpib As Single, conc_hpia As Single, conc_hpin As
Single

```

```

If (ConcHPOB.Text <> "") And (ConcHPOA.Text <> "") And _
(ConcHPON.Text <> "") And (ConcHPIB.Text <> "") And
(ConcHPIA.Text <> "") And _
(ConcHPIN.Text <> "") Then

Let conc_hpob = frmYourInput.ConcHPOB.Text
Let conc_hpoa = frmYourInput.ConcHPOA.Text
Let conc_hpon = frmYourInput.ConcHPON.Text
Let conc_hpib = frmYourInput.ConcHPIB.Text
Let conc_hpia = frmYourInput.ConcHPIA.Text
Let conc_hpin = frmYourInput.ConcHPIN.Text

DOC = conc_hpob + conc_hpoa + conc_hpon + conc_hpib +
conc_hpia + conc_hpin

thmfp_hpob = 7.53 * conc_hpob + 5.36
thmfp_hpoa = 3.85 * conc_hpoa + 6.83
thmfp_hpon = 17.22 * conc_hpon + 9.88
thmfp_hpib = 3.49 * conc_hpib + 8.37
thmfp_hpia = 23.46 * conc_hpia + 13.43
thmfp_hpin = 31.41 * conc_hpin + 10.1

total_thmfp = (thmfp_hpob + thmfp_hpoa + thmfp_hpon +
thmfp_hpib + thmfp_hpia + thmfp_hpin)

total_thmfp_corrected = total_thmfp * 0.13 + 4.74

'total_thmfp_corrected = total_thmfp

thmfp_hpob_corrected = 0.045 * total_thmfp_corrected

```

```

thmfp_hpoa_corrected = 0.068 * total_thmfp_corrected
thmfp_hpon_corrected = 0.157 * total_thmfp_corrected
thmfp_hpib_corrected = 0.072 * total_thmfp_corrected
thmfp_hpia_corrected = 0.464 * total_thmfp_corrected
thmfp_hpin_corrected = 0.194 * total_thmfp_corrected

frmToolkit.Show

frmToolkit.picResult.Cls

frmToolkit.picResult.Print "The THM FP for this sample is ";
Format(total_thmfp_corrected, "###0.000"); " ppb/DOC"

frmToolkit.picResult.Print ""

frmToolkit.picResult.Print "The THM FP for HPOB      is ";
Format(thmfp_hpob_corrected, "###0.000"); " ppb/DOC"

frmToolkit.picResult.Print "The THM FP for HPOA      is ";
Format(thmfp_hpoa_corrected, "###0.000"); " ppb/DOC"

frmToolkit.picResult.Print "The THM FP for HPON      is ";
Format(thmfp_hpon_corrected, "###0.000"); " ppb/DOC"

frmToolkit.picResult.Print "The THM FP for HPIB      is ";
Format(thmfp_hpib_corrected, "###0.000"); " ppb/DOC"

frmToolkit.picResult.Print "The THM FP for HPIA      is ";
Format(thmfp_hpia_corrected, "###0.000"); " ppb/DOC"

frmToolkit.picResult.Print "The THM FP for HPIN      is ";
Format(thmfp_hpin_corrected, "###0.000"); " ppb/DOC"

frmToolkit.picResult.Print ""

```

```

Else

frmErrorMessage.Show

frmErrorMessage.picError.Cls

frmErrorMessage.picError.Print "You Must First Compute"

frmErrorMessage.picError.Print "Concentration of ALL of the
Fractions"

End If

End Sub

Private Sub cmdHAAFP_Click()

Dim DOC As Single, conc_hopb As Single, conc_hpoa As Single,
conc_hpon As Single

Dim conc_hpib As Single, conc_hpia As Single, conc_hpin As
Single

If (ConcHPOB.Text <> "") And (ConcHPOA.Text <> "") And _
(ConcHPON.Text <> "") And (ConcHPIB.Text <> "") And
(ConcHPIA.Text <> "") And _
(ConcHPIN.Text <> "") Then

Let conc_hpob = frmYourInput.ConcHPOB.Text

Let conc_hpoa = frmYourInput.ConcHPOA.Text

Let conc_hpon = frmYourInput.ConcHPON.Text

Let conc_hpib = frmYourInput.ConcHPIB.Text

Let conc_hpia = frmYourInput.ConcHPIA.Text

Let conc_hpin = frmYourInput.ConcHPIN.Text

```

```

DOC = conc_hpob + conc_hpoa + conc_hpon + conc_hpib +
conc_hpia + conc_hpin
haafp_hpob = 0.49 * conc_hpob + 0.17
haafp_hpoa = 4.34 * conc_hpoa - 0.68
haafp_hpon = 48.4 * conc_hpon - 3.52
haafp_hpib = 0.66 * conc_hpib + 0.27
haafp_hpia = 0.6 * conc_hpia + 2.6
haafp_hpin = 3.11 * conc_hpin + 0.89
total_haafp = (haafp_hpob + haafp_hpoa + haafp_hpon +
haafp_hpib + haafp_hpia + haafp_hpin) / DOC
total_haafp_corrected = total_haafp * 1.04 - 7.56
'total_haafp_corrected = total_haafp
haafp_hpob_corrected = 0.106 * total_haafp_corrected
haafp_hpoa_corrected = 0.184 * total_haafp_corrected
haafp_hpon_corrected = 0.426 * total_haafp_corrected
haafp_hpib_corrected = 0.083 * total_haafp_corrected
haafp_hpia_corrected = 0.066 * total_haafp_corrected
haafp_hpin_corrected = 0.135 * total_haafp_corrected
frmToolkit.Show
frmToolkit.picResult.Cls
frmToolkit.picResult.Print "The HAA FP for this sample is ";
Format(total_haafp_corrected, "###0.000"); " ppb/DOC"
frmToolkit.picResult.Print ""

```

```

frmToolkit.picResult.Print "The HAA FP for HPOB      is ";
Format(haafp_hpob_corrected, "###0.000"); " ppb/DOC"

frmToolkit.picResult.Print "The HAA FP for HPOA      is ";
Format(haafp_hpoa_corrected, "###0.000"); " ppb/DOC"

frmToolkit.picResult.Print "The HAA FP for HPON      is ";
Format(haafp_hpon_corrected, "###0.000"); " ppb/DOC"

frmToolkit.picResult.Print "The HAA FP for HPIB      is ";
Format(haafp_hpib_corrected, "###0.000"); " ppb/DOC"

frmToolkit.picResult.Print "The HAA FP for HPIA      is ";
Format(haafp_hpia_corrected, "###0.000"); " ppb/DOC"

frmToolkit.picResult.Print "The HAA FP for HPIN      is ";
Format(haafp_hpin_corrected, "###0.000"); " ppb/DOC"

frmToolkit.picResult.Print ""

Else

frmErrorMessage.Show

frmErrorMessage.picError.Cls

frmErrorMessage.picError.Print "You Must First Compute"

frmErrorMessage.picError.Print "Concentration of ALL of the
Fractions"

End If

End Sub

Private Sub cmdHANFP_Click()

If (ConcHPOB.Text <> "") And (ConcHPOA.Text <> "") And _

```

```

(ConcHPON.Text <> "") And (ConcHPIB.Text <> "") And
(ConcHPIA.Text <> "") And _
(ConcHPIN.Text <> "") Then

Let conc_hpob = frmYourInput.ConcHPOB.Text
Let conc_hpoa = frmYourInput.ConcHPOA.Text
Let conc_hpon = frmYourInput.ConcHPON.Text
Let conc_hpib = frmYourInput.ConcHPIB.Text
Let conc_hpia = frmYourInput.ConcHPIA.Text
Let conc_hpin = frmYourInput.ConcHPIN.Text

hanfp_hpob = 0.5 * conc_hpob + 1.93
hanfp_hpoa = 1.85 * conc_hpoa + 1.91
hanfp_hpon = 1.17 * conc_hpon + 0.6
hanfp_hpib = 1.42 * conc_hpib + 2.14
hanfp_hpia = 0.3 * conc_hpia + 0.47
hanfp_hpin = 1.18 * conc_hpin + 2.33

total_hanfp = hanfp_hpob + hanfp_hpoa + hanfp_hpon +
hanfp_hpib + hanfp_hpia + hanfp_hpin

'total_hanfp_corrected = total_hanfp * 0.0749 + 1.5193
total_hanfp_corrected = total_hanfp

hanfp_hpob_corrected = 0.148 * total_hanfp_corrected
hanfp_hpoa_corrected = 0.205 * total_hanfp_corrected
hanfp_hpon_corrected = 0.194 * total_hanfp_corrected
hanfp_hpib_corrected = 0.128 * total_hanfp_corrected

```

```

hanfp_hpia_corrected = 0.173 * total_hanfp_corrected
hanfp_hpin_corrected = 0.153 * total_hanfp_corrected

frmToolkit.Show

frmToolkit.picResult.Cls

frmToolkit.picResult.Print "The HAN FP for this sample is ";
Format(total_hanfp_corrected, "###0.000"); " ppb/DOC"

frmToolkit.picResult.Print ""

frmToolkit.picResult.Print "The HAN FP for HPOB      is ";
Format(hanfp_hpob_corrected, "###0.000"); " ppb/DOC"

frmToolkit.picResult.Print "The HAN FP for HPOA      is ";
Format(hanfp_hpoa_corrected, "###0.000"); " ppb/DOC"

frmToolkit.picResult.Print "The HAN FP for HPON      is ";
Format(hanfp_hpon_corrected, "###0.000"); " ppb/DOC"

frmToolkit.picResult.Print "The HAN FP for HPIB      is ";
Format(hanfp_hpib_corrected, "###0.000"); " ppb/DOC"

frmToolkit.picResult.Print "The HAN FP for HPIA      is ";
Format(hanfp_hpia_corrected, "###0.000"); " ppb/DOC"

frmToolkit.picResult.Print "The HAN FP for HPIN      is ";
Format(hanfp_hpin_corrected, "###0.000"); " ppb/DOC"

frmToolkit.picResult.Print ""

Else

frmErrorMessage.Show

frmErrorMessage.picError.Cls

```

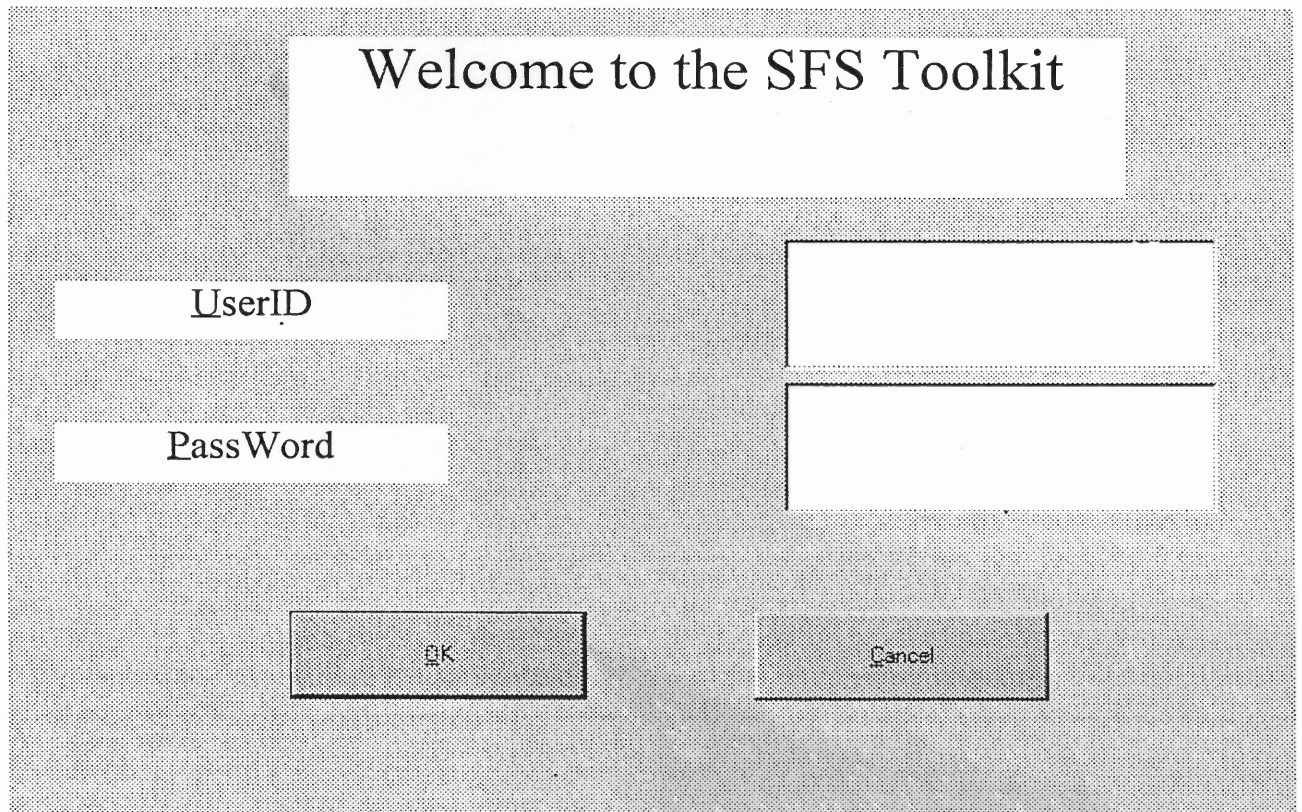


```
frmErrorMessage.picError.Print "You Must First Compute"
```

```
frmErrorMessage.picError.Print "Concentration of ALL of the  
Fractions"
```

```
End If
```

```
End Sub
```



>Welcome to the SFS Toolkit

UserID

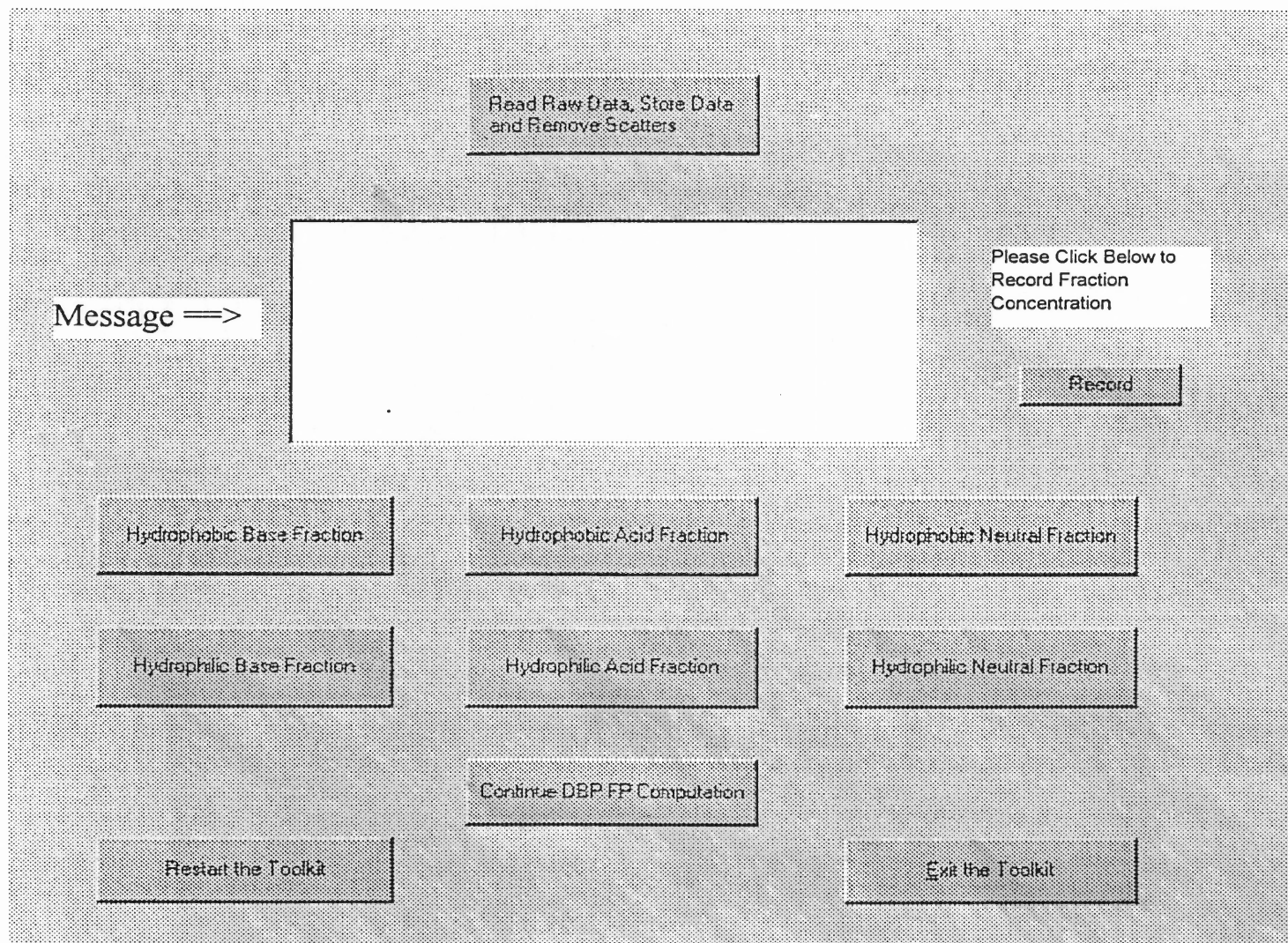
PassWord

OK

Cancel

The image shows a login window titled "Welcome to the SFS Toolkit". It features two input fields on the right side, one for "UserID" and one for "PassWord", each preceded by a label on the left. At the bottom, there are two buttons: "OK" and "Cancel". The entire window has a light gray background with a fine grid pattern.

Signon Screen



The image shows the SFS Toolkit Main Screen, which is a graphical user interface for data analysis. It features a central white rectangular area for displaying data or messages. Above this area is a button labeled "Read Raw Data, Store Data and Remove Scatters". To the left of the central area is a label "Message ==>" followed by a right-pointing arrow. To the right of the central area is a text box containing the instruction "Please Click Below to Record Fraction Concentration" and a button labeled "Record". Below the central area, there are several buttons arranged in a grid. The first row contains three buttons: "Hydrophobic Base Fraction", "Hydrophobic Acid Fraction", and "Hydrophobic Neutral Fraction". The second row contains three buttons: "Hydrophilic Base Fraction", "Hydrophilic Acid Fraction", and "Hydrophilic Neutral Fraction". The third row contains two buttons: "Continue DBP FP Computation" (centered) and "Exit the Toolkit" (right-aligned). The bottom row contains two buttons: "Restart the Toolkit" (left-aligned) and "Exit the Toolkit" (right-aligned).

Read Raw Data, Store Data and Remove Scatters

Message ==>

Please Click Below to Record Fraction Concentration

Record

Hydrophobic Base Fraction

Hydrophobic Acid Fraction

Hydrophobic Neutral Fraction

Hydrophilic Base Fraction

Hydrophilic Acid Fraction

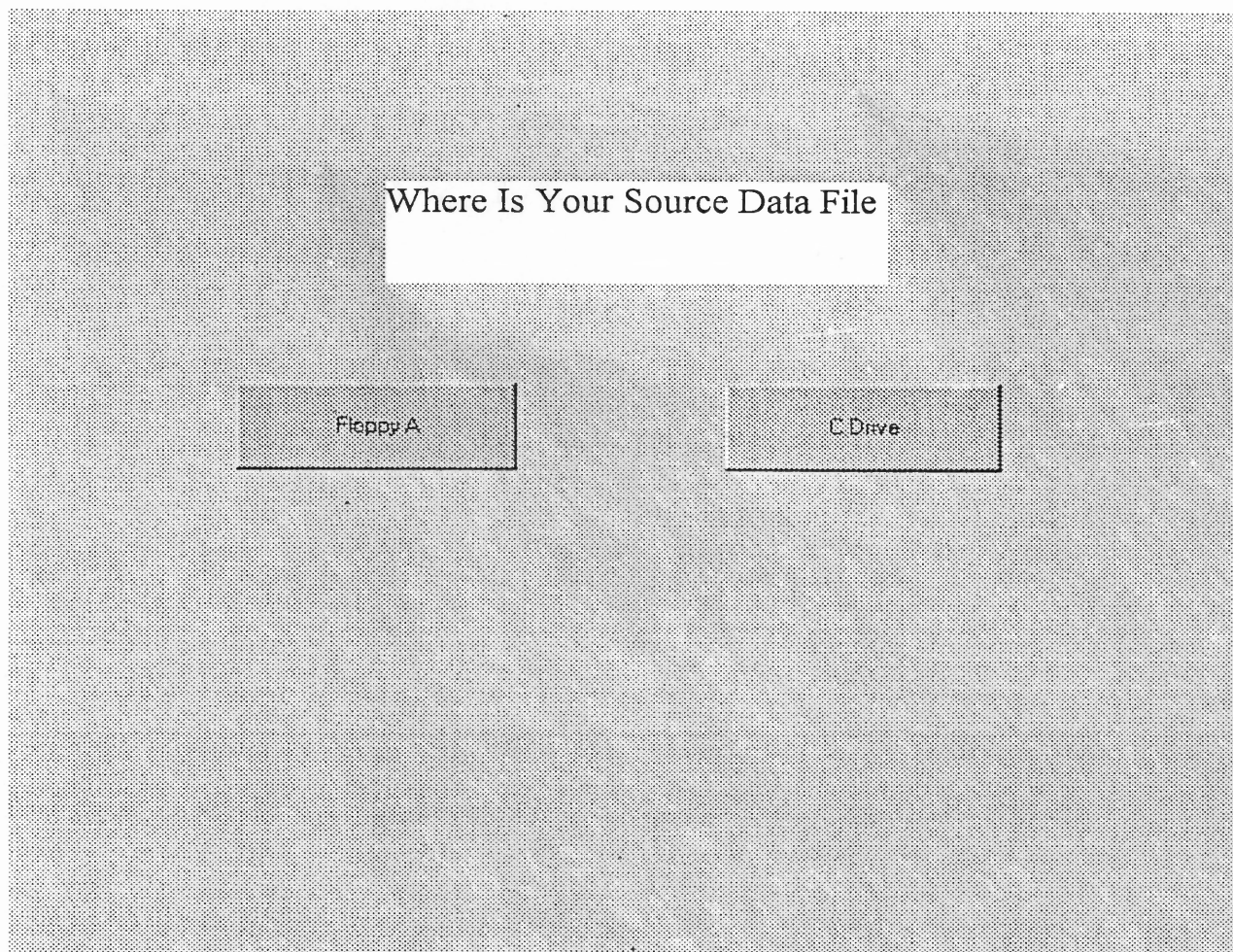
Hydrophilic Neutral Fraction

Continue DBP FP Computation

Restart the Toolkit

Exit the Toolkit

SFS Toolkit Main Screen



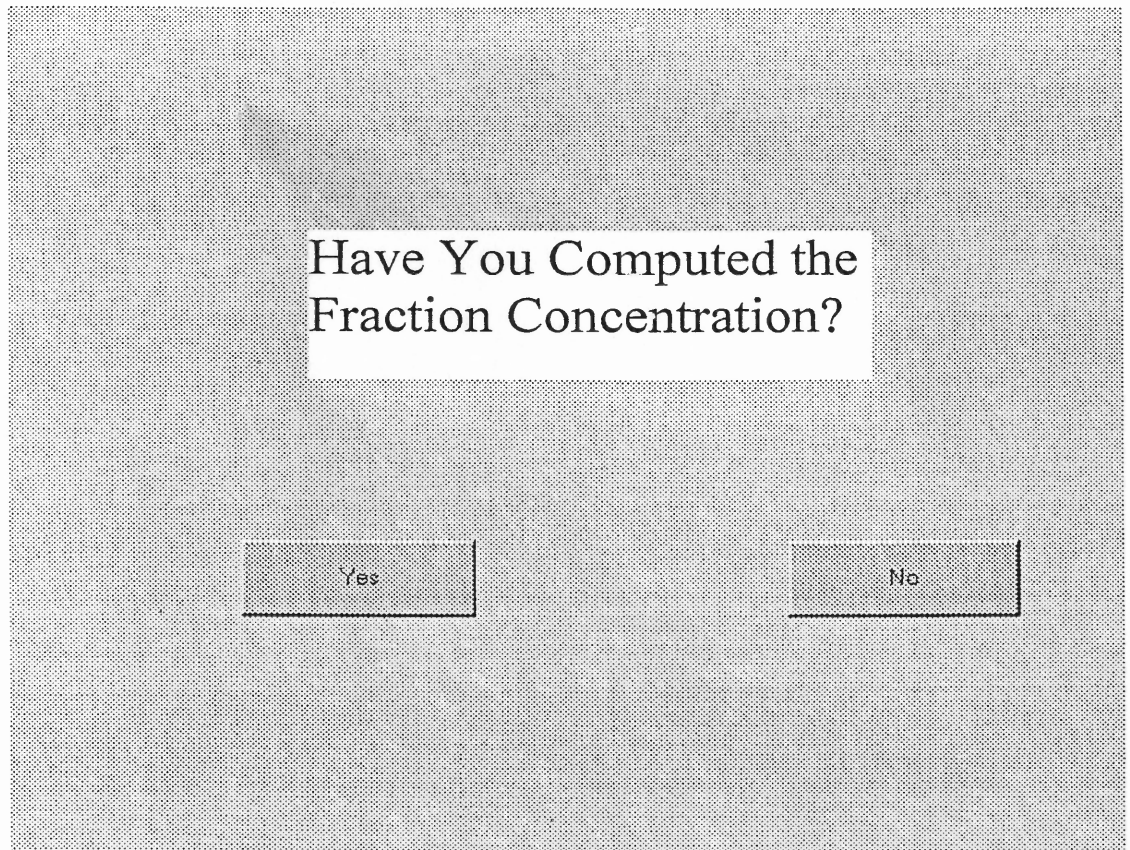
Screen to Select the Location of Data File to be Imported

Spectral Slope	
Spectral Area	
Shape Factor	
	Compute Concentration
	Compute DBP FP

Output Screen for Key Parameters

Please Enter the Concentration of the Hydrophobic Base Fraction	<input type="text"/>
Please Enter the Concentration of the Hydrophobic Acid Fraction	<input type="text"/>
Please Enter the Concentration of the Hydrophobic Neutral Fraction	<input type="text"/>
Please Enter the Concentration of the Hydrophilic Base Fraction	<input type="text"/>
Please Enter the Concentration of the Hydrophilic Acid Fraction	<input type="text"/>
Please Enter the Concentration of the Hydrophilic Neutral Fraction	<input type="text"/>
<input type="button" value="Back to Continue/Finish Computing Fraction Concentration"/>	
<input type="button" value="Compute THM FP"/>	<input type="button" value="Compute HAA FP"/>

Screen Containing Input for the Computation of DBP FP

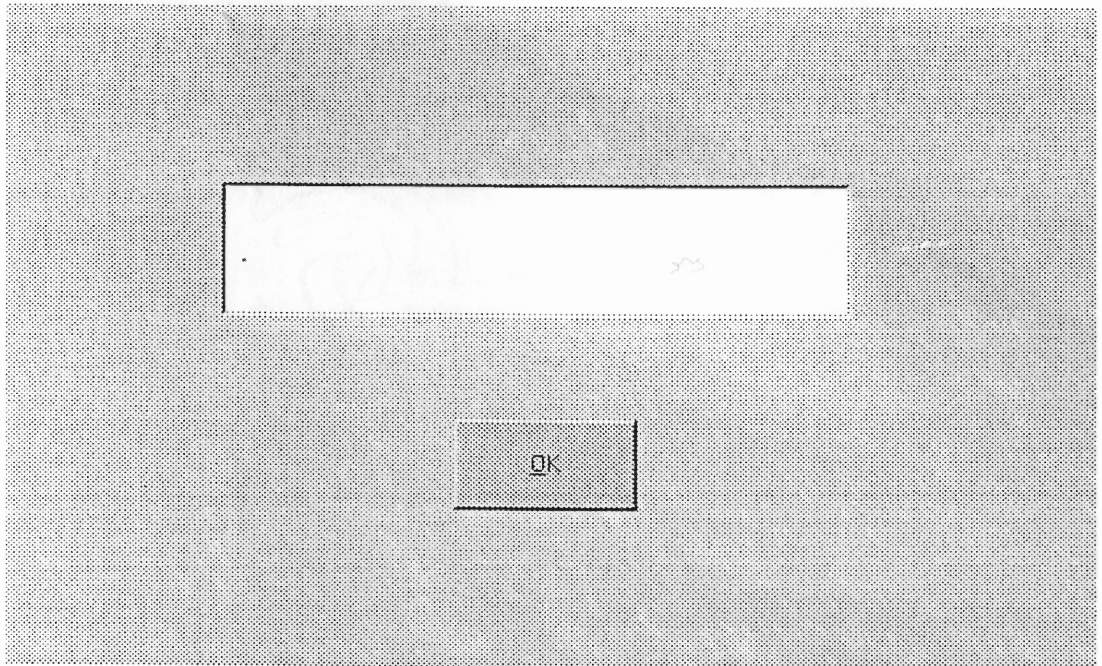


A dialog box with a light gray background and a thin black border. In the center, there is a white rectangular area containing the text "Have You Computed the Fraction Concentration?". Below this text, there are two buttons: "Yes" on the left and "No" on the right. Both buttons have a light gray background and a thin black border.

Have You Computed the
Fraction Concentration?

Yes No

Reminder Message Board



General Error Message Board

REFERENCES

- Aiken G. and Leenheer J (1993) Isolation and chemical characterization of dissolved and colloidal organic matter. *Chemistry and Ecology* **8**, 135-151.
- Amin S. and Jayson G.G (1996) Humic substance uptake by hydrotalcites and pilcs. *Wat. Res.* **30**, 299-306.
- Amiri A. S., Bolton J.R. and Cater, S.R. (1997) Ferrioxalate-mediated photodegradation of organic pollutants in contaminated water. *Wat. Res.* **31**, 787-798.
- Amy G. L. (1993) Using NOM characterization for the evaluation of treatment in *Proceedings of Natural Organic Matter in Drinking Water—Origin, Characterization, and Removal Workshop*, AWWA Res. Found., Chamonix, France (September 19-22).
- Amy G.L., Chadik P.A. and Chowdhury Z.K (1987) Developing models for predicting trihalomethane formation potential and kinetics. *J. AWWA* **79**, 89-97.
- Amy G. L., Siddiqui M., Zhai W., DeBroux J., and Odem, W. (1995) *National Survey of Bromide Ion in Drinking Water Sources and Impacts on Disinfection By-Product Formation*. AWWA Res. Found., Denver, CO.
- AWWA Res. Found. (1982) *Treatment Techniques for Controlling Trihalomethanes in Drinking Water*. Denver, CO.
- Babichenko S., Lapimaa J, Poryvkina L. and Varlamov V. (1995) On-line fluorescent techniques for diagnostics of water environment. *SPIE* **2503**, 157-161.
- Belin C., Quéllec C., Lamotte M., Ewal M. and Simon P. (1993) Characterization by fluorescence of the DOM in natural water. Application to fractions obtained by tangential ultrafiltration and XAD resin isolation. *Env. Tech.* **14**, 1131-1144.
- Becker W. and O'Melia C. (1996) Ozone, oxalic acid, and organic matter molecular weight - effects on coagulation. *Ozone: Science and Engineering* **18**, 311-324.
- Bose P., Bezbarua B. K. and Reckhow D. A. (1994) Effect of ozonation on some physical and chemical properties of aquatic natural organic matter. *Ozone: Science & Engineering* **16**, 89-112.
- Bruchet A., Rousseau C. and Mallevialle J. (1990) Pyrolysis-GC-MS for investigating high-molecular-weight THM precursors and other refractory organics. *J. AWWA*. **82**, 66-74.

- Bruchet A., Anselme C., Duguet J. P. and Mallevialle J. (1987) THM formation potential and organic content: a new analytical approach in water chlorination chemistry. *Environmental Impact and Health Effects* **6**, 633-647.
- Chapra S., Canale R. and Amy G. (1997) Empirical models for disinfection by-products in lakes and reservoirs. *J. Env. Engineering* **123** (7), 714-715.
- Chen P.T. and Rest G. B. (1996) Disinfection by-products-- the techniques of control. *Public Works* **127**, 36-38.
- Chubarov V., Fadeev V., Filippova E.M. (1994) Laser diagnostics of natural and pollution organic complexes in water environment. *Laser Application in Life Sciences* **2370**, 527-631.
- Collins M. R., Amy G. L. and Steelink C. (1986) Molecular weight distribution, carboxylic acidity, and humic substances content of aquatic organic matter: implications for removal during water treatment. *Environmental Sci. Technol.* **20**, 1028-1032.
- Cowman G. A. and Singer P. C. (1994) Effect of bromide ion on haloacetic acid speciation resulting from chlorination and chloramination of aquatic humic substances." *Env. Sci. & Technol.* **30**, 16-24.
- Crum R.H., Murphy E.M., and Keller C.K. (1996) Non-adsorptive method for the isolation and fractionation of natural dissolved organic carbon. *Wat. Res.* **30**, 1304-1311.
- Croue J. P., Martin B., Simon P. and Legube B. (1993) Les matieres hydrophobes et hydrophiles des eaux de retenue- extraction, caracterisation et quantification. *Water Supply* **11**, 79-90.
- Crozes G., White P. and Mashall M. (1995) Enhanced coagulation: its effect on NOM removal and chemical costs. *J. AWWA* **87**, 78-89.
- Crum R.H., Murphy E. M. and Keller C. K. (1996) Non-adsorptive method for the isolation and fractionation of natural dissolved organic carbon. *Wat. Res.* **30**, 1304-1311.
- Day G. McD., Beckett R., Hart B. and McKelvie I. (1991) Characterization of natural organic matter from four victorian freshwater systems. *Aust. J. Mar. Freshwater Res.* **42**, 675-687.
- Eggins B.R., Palmer F.L. and Byrne J.A. (1997) Photocatalytic treatment of humic substances in drinking water. *Wat. Res.* **31**, 1223-1226.

- Hautman D. P. and Bolyard M. (1992) Using ion chromatography to analyze inorganic disinfection by-products. *J. AWWA*. **84**, 88-93.
- Hofmann R. and Andrews R.C. (1996) An economical experimental approach to developing disinfection by-product predictive models in *Water Disinfection and Natural Organic Matter: Characterization and Control*. American Chemical Society, Washington, D.C.
- Huang J and Smith G. Spectrophotometric determination of total trihalomethanes in finished waters. *J. AWWA*. **76**, 168-171.
- Harrington G. W., Bruchet A., Rybacki D. and Singer P.C. (1996) Characterization of natural organic matter and its reactivity with chlorine. *Water Disinfection and Natural Organic Matter: Characterization and Control* (Edited by Minear, R. and Amy, G). American Chemical Society, Washington, D.C.
- Hautman D. P. and Bolyard M. (1992) Using ion chromatography to analyze inorganic disinfection by-products. *J. AWWA*. **84**, 88-93.
- Hofmann R. and Andrews R.C. (1996) An economical experimental approach to developing disinfection by-product predictive models. *Water Disinfection and Natural Organic Matter: Characterization and Control* (Edited by Minear, R. and Amy, G). American Chemical Society, Washington, D.C.
- Jacangelo J.G., DeMarco J., Owen D.M. and Randtke S.J. (1995) Selected processes for removing NOM: an overview. *J. AWWA*. **87**, 64-77.
- Kaitals S., Babichenko S., Poryvkina L. and Lasbas A. (1995) Fluorescent analysis of pigment composition of natural phytoplankton. *J. MTS*. **28**, 50-58.
- Kalle (1949) *Marine Chemistry* **47**, 127-144.
- Kochar I. (1998) Fluorescence spectroscopy for the characterization of humic and fulvic acids and their disinfection by-products formation potential. *M.S. thesis, Department of Civil and Environmental Engineering, NJIT, Newark, NJ*.
- Korshin G.V., Li C-H. and Benjamin M.M. (1997) The decrease of UV absorbance as an indicator of TOX formation. *Wat. Res.* **31**, 946-949.
- Korshin G. V., Benjamin M. M. and Sletten R. S. (1997) Adsorption of natural organic matter (NOM) on iron oxide: effects on NOM composition and formation of organo-halide compounds during chlorination. *Wat. Res.* **31**, 1643-1650.

- Krasner S. W., McGuire M. J., Jacangelo J. G., Patania N. L., Reagan K. M. and Aieta E. M. (1989) Occurrence of disinfection by-product in US drinking water. *J. AWWA*, **81**, 41-53.
- Krasner S.W, Croue J.P., Buffle J. and Perdue E.M. (1996) Three approaches for characterizing NOM. *J. AWWA*, **88**, 66-79.
- Leenheer J. A. (1981) Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters. *Environ. Sci. Technol.* **15**, 578-587.
- Loge F., Darby J. L. and Tchobanoglous G. (1996) UV disinfection of wastewater: probabilistic approach to design. *J. Env. Engineering*, **122**, 1078-1084.
- Lykins B.W., Koffskey W.E. and Patterson K.S. (1994) Alternative disinfectants for drinking water treatment. *J. Env. Engineering* **120** (4): 745-758.
- Mallevalle J. (1993) Why is natural organic matter problematic? In *Proceedings of Natural Organic Matter in Drinking Water—Origin, Characterization, and Removal Workshop*, AWWA Res. Found., Chamonix, France (September 19-22).
- Martin B., Croue J. P., Lefebvre E. and Legube B. (1997) Distribution and characterization of dissolved organic matter of surface waters. *Wat. Res.* **31**, 541-553.
- Marhaba T. F. and Washington M. B. (1998) Drinking water protection and by-products: history and current practice. *Advances in Environmental Research* **2**, 103-115.
- Marhaba T. F., Van D. and Lippincott R. L. (1998) Effects of ozonation vs. chlorination water treatment operations on natural organic matter fractions. In *Proceedings of the 1998 Int. Ozone Assoc. Ann. Conf.*, pp. 363-382, Vancouver, B.C, Canada
- Marhaba T.F., Van D. and Lippincott R.L. (1999) Characterizing dissolved organic matter fractions using spectral fluorescent signatures and post processing by principal component analysis. *Fresenius's Analytical Chemistry*. Accepted for publication.
- Marhaba T.F. and Van D. (1999) Chlorinated disinfection by-product formation potential of dissolved organic matter fractions at an ozonation water treatment plant. *Advanced Environmental Research* **3** (3), 255-268.
- Marhaba T.F., Van D. and Lippincott R.L. (1999) Changes in NOM fractionation through treatment: a comparison of ozonation and chlorination. *Ozone Sci Eng.* Accepted for publication.

- Marhaba T.F., Van D. and Lippincott R.L. (1999) Rapid identification of dissolved organic matter fractions in water by spectral fluorescent signatures. *Wat. Res.* Accepted for publication.
- Pipanda N. (1999) Coagulation and disinfection by-products formation potential of dissolved organic matter fractions. *M.S. thesis, Department of Civil and Environmental Engineering, NJIT, Newark, NJ.*
- Mayohealth (1999) The bug that made Milwaukee famous. Web site address: www.mayohealth.org/mayo/9606/htm/cryptpsp.htm
- McClellan J.N., Reckhow D.A., Tobiason J.E., Edzwald J.K. and Hess A.F. (1996) Empirical models for chlorination by-products: four years of pilot experience in Southern Connecticut in *Water Disinfection and Natural Organic Matter: Characterization and Control*. American Chemical Society, Washington, D.C.
- Mescape (1998) Study links miscarriage to water. Web site address: news.medscape.com/jobson/medtrib/obgyn/1998/v05.n04/studylinksmiscarriageto wat.html
- Minear R. A. and Bird J. C. (1980) Trihalomethanes: impact of bromide ion concentration on the yield, species distribution, rate of formation, and influence of other Variables. In *Water Chlorination, Environmental Impact and Health Effects* (Edited by Jolley R.), Vol. 3. Ann Arbor, Michigan: Ann Arbor Sci.
- Minear R. and Amy G. (1996) Water disinfection and natural organic matter: history and overview. In *Water Disinfection and Natural Organic Matter: Characterization and Control*. American Chemical Society, Washington, D.C.
- Mongomery W. *Final Report: Mathematical Modeling of the Formation of THMs and HAAs in Chlorinated Waters*. AWWA Res. Found, Denver, CO.
- Morrow C. M. and Minear R. A. (1987) Use of regression models to link raw water characteristics to trihalomethane concentrations in drinking water. *Wat. Res.* **21**, 41-48.
- Najm I.N., Patania N.L., Jacangelo J.G. and Krasner S.W. (1994) Evaluating surrogates for disinfection by-products. *J. AWWA* **86**, 98-106.
- New Jersey Department of Environmental Protection. *Special Water Treatment Study-Phase I Final Report*. (1983)
- Newcombe G., Drikas M., Assemi S. and Beckett R. (1997) Influence of characterized natural organic material on activated carbon adsorption: I. characterization of concentrated reservoir water. *Wat. Res.* **31**, 965-972.

- Nieminski E.C., Chaudhuri S., Flint T.I., Paxman S.W., Reynolds F.P. and Carman (1996) ICR Survival Guide. *J. AWWA* **86**, 50-63.
- Orlov Y., Persiantsev I., Rebrik S. and Babichenko S. (1995) Application of neural networks to fluorescent diagnostics of organic pollution in water. *Inter. Society for Optical Engineering Air Toxics and Water Monitoring*. **2503**, 150-156.
- Owen D. M., Amy G. L., Chowdhury Z. K., Paode R., McCoy G. and Viscosil K. (1995) NOM characterization and treatability. *J. AWWA*. **87**, 47-63.
- Owen D. M., Amy G. L. and Chowdhury Z. K. (1993) *Characterization of Natural Organic Matter and its Relationship to Treatability*. AWWA Res. Found., Denver, CO.
- Reckhow D. A. and Singer P. C. (1990) Chlorination by-products in drinking waters: from formation potentials to finished water concentrations. *J. AWWA* **82**, 173-180.
- Reckhow D. A. and P. C. Singer (1985) *Water Chlorination: Chemistry, Environmental Impact and Health Effects* (Edited by Jolley R., Bull R. J., Davis W. P., Katz S., Roberts M. H. and Jacobs V. A.), **5**:1229-1257, Lewis Publishers, Chelsea, MI.
- Reckhow D.A. and Singer, P.C. (1990) Chlorination by-products in drinking waters: from formation potentials to finished water concentrations. *J. AWWA* **82**, 173-180.
- Reynolds T.D. and Richards P.A. (1996) *Unit operations and processes in environmental engineering*. PWS Publishing Company, Boston, MA.
- Rice R. G. (1980) The Use of ozone to control trihalomethanes in drinking water Treatment. *Ozone: Science & Engineering* **2**, 75-99.
- Richardson S.D., Thruston A.D. and Collette. (1994) Multispectral identification of chloride dioxide disinfection by-products in drinking water. *Env. Sci. Tech.* **28** (4): 592-599.
- Roberson J.A., Cromwell III, Krasner, M.J., McGuire, Owen D.M., Regli S. and Summers R.S. (1995) The D/DBP rule: where did the numbers come from? *J. AWWA* **87**, 46-57.
- Rook J. J. (1977) Chlorination reactions of fulvic acids in natural waters. *Environ. Sci. Technol.* **11**: 478-482.
- Sawyer C.N. and McCarty P.L. (1978) *Chemistry for environmental engineering*. McGraw-Hill, Inc., NY.

- Senesi N. (1990) Molecular and quantitative aspects of the chemistry of fulvic acid and its interactions with metal ions and organic chemicals-- the fluorescence spectroscopy approach. *Analytica Chimica* **232**, 77-106.
- Senesi N., Miano T., Provenzano M. and Brunetti G. (1989) Spectroscopic and compositional comparative characterization of I.H.S.S. reference and standard fulvic and humic acids of various origin. *The Science of the Total Environment*. **81/82**, 143-156.
- Schnitzer M. and Khan S. U. (1978) Eds., *Soil Organic Matter*. New York: Elsevier.
- Shukairy H.M., Miltner R.J. and Summers R.S. (1995) Bromide's effect on DBP formation, speciation and control: Part 2, Biotreatment. *J. AWWA* **87**, 71-82.
- Schnoor J. L., Nitzschke J. L., Lucas R. D. and Veenstra J.N. (1979) Trihalomethane yields as a function of precursor molecular weight. *Environ. Sci. Technol.* **13**, 1134-1138.
- Scully F. E., Howell G. D., Kravitz R., Jewell J. T., Hahn V. and Speed M. (1988) Proteins in natural waters and their relation to the formation of chlorinated organics during water disinfection. *Environ. Sci. Technol.* **22** (5), 537-542.
- Standard Methods for the Examination of Water and Waste Water* (1995), 16th Edition, APHA, AWWA, and WPCF, Washington, DC
- Sierra M., Donard O., Lamotte M., Belin C. and Ewald M. (1994) Fluorescence spectroscopy of coastal and marine waters. *Marine Chemistry* **47**, 127-144.
- Singer P.C. (1994) Control of disinfection by-products in drinking water. *Jour. Env. Engineering* **120**, 727-744.
- Sternstein M. (1994) *Statistics*. Barron's Educational Series, NY.
- Singer P.C. and Chang S.D. (1989) Correlations between trihalomethanes and total organic halides formed during water treatment. *J. AWWA* **81**, 61-65.
- Symons J., Krasner S., Simms L. and Scilimenti M. (1993) Measurement of THM and precursor concentrations revisited: the effect of bromide ion. *J. AWWA* **85**, 51-62.
- Thurman E. M. (1985) Development in biochemistry. In *Organic Geochemistry of Natural Waters* (Edited by Thurman E.M), M. Nijhoff/ Dr. W. Junk Publisher, Dordrecht, Netherlands.
- Thurman E.M. and Malcolm R.L. (1981) Preparative isolation of aquatic humic substances. *Environmental Science & Technology* **15**, 463-466.

Tipson R. S. NBS Monogr. (U.S.) (1968) No. 110.

USEPA (1998) National Primary Drinking Water Regulations: Disinfectants and Disinfection ByProducts. Final Rule. Fed. Register 63(241), 69389-69476 December 16.

USEPA (1994) National Primary Drinking Water Regulations: Enhanced Surface Water Treatment Rule (ESWTR). Federal Register 59:38832 July 29.

Washington M. (1998) Fluorescence spectroscopy for the characterization of total organic carbon and disinfection by-product formation. *M.S. thesis, Department of Civil and Environmental Engineering, NJIT, Newark, NJ.*

Waternews (1999) Chlorination. Web site address:
www.clo2.com/reading/waternews/newchlorination.html

Weber W.J. (1972) *Physicochemical Process for Water Quality Control*. John Wiley & Son

White C.E. and Argauer R. (1970) *Fluorescence Analysis; A practical approach*. M. Dekker, NY